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Evaluation Guidelines for Toxic Air Emissions from Land Disposal Facilities Technical Resource Document for Air Emissions, Monitoring and Control

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Air Emissions, Monitoring and control

EVALUATION GUIDELINES
FOR TOXIC AIR EMISSIONS
·FROM LAND DISPOSAL FACILITIES

Office of Solid Waste
U.S. Environmental Protection Agency
Washington, D.C.

August, 1981

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This manual presents procedures for assessing the impact of Hazardous Air Emissions from disposal facilities on the downwind population for Air Monitoring, and for Evaluating the control techniques for treating toxic chemicals.

The report is prepared to provide guidance to the facility owner or operator and the permit writer on evaluating the performance of facility design and preparation and analysis of the permit application.

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FOREWORD

This manual presents procedures for assessing the impact of hazardous air emissions from disposal facilities on the downwind population, for air monitoring, and for evaluating the control techniques for treating toxic chemicals. The disposal facilities considered in this document include surface impoundments, seepage facilities, landfills, and land treatment facilities. The application of the procedure may be extended to waste piles depending upon the similarity of air emissions routes and the characteristics of the emitting surface in contact with the atmosphere. These facilities will hereinafter be referred to as disposal facilities or land disposal facilities.

The report is prepared to provide guidance to the facility owner or operator and the permit writer on evaluating the performance of facility design, and preparation and analysis of the permit application. The manual consists of three parts. Part A will provide a quantitative tool for the rational evaluation of hazardous air emissions from land disposal facilities, and for prediction of ambient air quality of hazardous waste components. Part B presents methods of monitoring organics in the ambient air. Part C describes the method of analyzing treatment techniques that can be used to remove volatile chemicals from the waste.

Chapter 2 of Part A presents the method of estimating the hazardous air technique for predicting ambient air quality. Chapter 3 of Part B describes a screening technique for predicting ambient air quality. The preliminary evaluation by the screening technique will form a basis for requiring a more sophisticated evaluation of the impact of the disposal facilities.

Chapter 4 of Part A is an attempt to gather data on the present background concentrations of hazardous chemicals in urban and rural ambient air. The background concentration will affect the extent of emission control required for prevention of adverse health effect on the downwind public. A logical source of such information would be site-specific monitoring data. The example calculations presented in Chapter 6 will serve as a quick reference for the use of the analytical techniques.

CONTENTS

PAGE

Part A Emission Estimation and Risk Analysis 1

I. INTRODUCTION 1

II. ESTIMATION OF EMISSION RATES FROM DISPOSAL FACILITIES. 5

- 1. Surface Impoundments 5
- 2. Landfills 16
- 3. Land Treatment Facilities 21

III. AMBIENT AIR QUALITY MODELING FOR AREA SOURCES 25

IV. EVALUATION OF EXPOSURE CONCENTRATION 32

V. CONTROL TECHNOLOGIES 50

V. EXAMPLE CALCULATIONS 51

- 1. Estimation of Emission Rates from Surface Impoundments 51
- 2. Estimation of Emissions from the Biological Treatment System when only the influent concentration is known 53
- 3. Estimation of Emissions Rates from Landfills 55
- 4. Estimation of Emission Rates from Land Treatment Facilities 60
- 5. Dispersion Modeling-Screening Technique 63
- 6. Consideration of Other Health Criteria 66

VII. REFERENCES 75

APPENDICES 77

- A. Methods for Determining K-Values 78
- B. A Model for Volatile Chemical Emissions to Air from Landfarming of Oily Wastes 84
- C. Summary of Data used in Obtaining Mass Transfer Coefficients in Table 1 96
- D. Unit Risks Calculated from Ingestion Study Potency Slope 97
- E. Multimedia Rate Constants 99
- F. Conversion of Mass Transfer Coefficients 108

		PAGE
Part B	Emission Monitoring and Measurements	109
I.	AMBIENT AIR MONITORING	109
	1. Analytical Protocol for Organic Compounds	109
	2. Analytical Protocol for Trace Particulates	137
II.	EMISSION RATE MEASUREMENTS	143
Part C	Control Technologies	153
I.	STEAM STRIPPER	153
II.	SOLVENT EXTRACTION	183

LIST OF TABLES

Table No.	Title	Page
1.	Mass Transfer Coefficients for Reference Compounds	11
2.	List of Chemicals Assessed Weight of Carginogenic Evidence	33
3.	Ambient Air Concentrations of Probable Carcinogens	38
4.	Comparison of Ambient Air Concentrations and Maximum Allowable Concentrations	42
5.	Hazardous Organic Vapors and Particulate Trace Metals in Ambient Air at Hazardous Waste Facilities	48

PART A
EMISSION ESTIMATION AND RISK ANALYSIS

INTRODUCTION

1.1 Purpose

Part A of the guidance manual is prepared to present a brief description of technical information that can be used in evaluating the potential of emissions of volatile hazardous chemicals into the atmosphere from land disposal facilities. The land disposal facilities include surface impoundments, seepage facilities, landfills, and land treatment facilities. The method for predicting the impact of the facility on ambient air quality essentially consists of two step processes; first, it requires estimation of emission rates of toxic components from a land disposal facility; second, this information is in turn used for air dispersion modeling to predict the ambient air quality.

1.2 Content Description

The dispersion modeling technique is rather general to the extent that it is applicable to area sources of which land disposal facilities are a type. The estimation of emission rates, however, requires a particular method that is suited to each application of land disposal facilities. Although waste piles are not specifically covered in this report, it is believed that one of the methods (most likely the land treatment model) may be used for the estimation of volatile emissions from waste piles based on the similarity of transport routes and configuration. In all cases the estimation method for the emission rates addresses volatile constituents in the waste. The particulate matter emissions are generally derived from the expression of "emission factors", but this aspect of emission rate estimation is not addressed in this report.

The techniques presented in Part A are predictive models, and do not involve the methods of actual measurements. The methods of performing measurements of emission rates as well as ambient air concentrations of waste constituents are addressed in Part B and these measurements may be effectively used to verify the accuracy of the prediction.

The land disposal facility should be designed, maintained and closed in a manner which will not impair post-closure uses of the land and soil, and public health will not be endangered due to air emissions and water infiltration. The procedure presented here will allow one to make a preliminary evaluation on the adequacy of design for a disposal facility from a standpoint of atmospheric dispersion of volatile hazardous chemicals. The evaluation examples will serve as a quick reference problem for estimating the emission rates and for comparing the estimated concentrations with the permit provisions.

The evaluation procedure can be used to check the adequacy of the facility design to minimize the potential of air emissions of hazardous substances as necessary to protect public health.

The main body of the report will address various models needed for the evaluation and predictions. Specific examples are shown in a later chapter to facilitate their use.

1.3 Use of Other Manuals

EPA has published a number of technical resource documents and manuals to support recently proposed RCRA regulations. Each document supports the appropriate area of concern. But some documents also contain references and a brief description of the subject matter related to air emissions. These documents and manuals include:

- Management of Hazardous Waste Leachate
- Guide to the Disposal of Chemically Stabilized and Solidified Wastes
- Closure of Hazardous Waste Surface Impoundments
- Design and Management of Hazardous Waste Land Treatment Facilities.
- Soil Permeability Test Manual
- Leachate Characterization from a Hazardous Waste Facility
- Landfill Closure Manual
- Ground-Water Monitoring for Owners and Operators of Treatment, Storage or Disposal Facilities
- Landfill and Surface Impoundment Performance Evaluation
- Evaluating Cover Systems for Solid and Hazardous Waste
- Guide to the Disposal of Chemically Stabilized and Solidified Wastes
- Hydrologic Simulation on Solid Waste Disposal Sites
- Management of Hazardous Waste Leachate
- Lining of Waste Impoundment and Disposal Facilities
- Design and Management of Hazardous Waste Land Treatment Facilities
- Closure of Hazardous Waste Surface Impoundments

This manual is not directly related to any of the above manuals. However, the reader is encouraged to consult the above documents for any materials relevant to the evaluation of air emissions.

The predictive models presented in this manual are based on the best information currently available in the literature. The

9<

correlations pertaining to the estimation of volatile emissions from surface impoundments are presently being tested in the field using the "concentration profile technique." In the models for estimating emissions from covered landfills, the diffusion in soil pore is considered a rate controlling step. The effect of barometric pumping and thermal diffusion on the rate of emissions has been mentioned in the literature. But the information is lacking on importance of these phenomena in comparison with diffusion controlling transport. The land treatment model is rather a recent endeavor and would require further experimental verification to identify all parameters affecting air emissions and to substantiate its accuracy.

II. ESTIMATION OF EMISSION RATES FROM DISPOSAL FACILITIES

A summary of estimation methods will be presented first. Explanation or derivation of the equations and some pertinent information will follow. Example calculations for using the estimation methods are shown in Section VI.

1. Surface Impoundments.

A. Summary of Estimating Equations

$$Qi = 4047 \times 10^4 \, MW_i \cdot K_{Li} \, \overline{A}_c \, x_i \qquad (1)$$

where Q_i : emission rate of chemical i, gr/sec

MW_i : emission rate of chemical, gr/sec

K_{Li} : overall mass transfer coefficient of chemical i expressed in liquid phase concentration, grmol/cm^2. sec

$\overline{A}_c$: surface area of the impoundment expressed in acres (Suscript C denotes the convective area of the surface impoundment)

x_i : mole fraction of component i in the liquid phase

4047×10^4 : denotes the factor needed to convert the surface area expressed in acres to cm^2.

The overall mass transfer coefficients can be estimated from

$$\frac{1}{K_{Li}} = \frac{1}{k_{Li}} + \frac{1}{K_i \quad k_{gi}} \qquad (2)$$

where k_{Li} : individual liquid phase mass transfer coefficient of chemical i, grmol/cm^{2}sec.

k_{gi} : individual gas phase mass transfer coeeficient of chemical i, grmol/cm^{2}sec

K_i : vapor-liquid equilibrium constant of chemical i (this is equivalent to Henry's law constant applicable to low solubility compounds in aqueous solution), dimensionless obtained from $y_i = K_i x_i$, where y_i is the mole fraction of chemical i in the gas phase; See Appendix A for the estimation method.

The individual mass transfer coefficients can be estimated from Equations (6) and (8), presented later.

b. Description

In order for the hazardous compound in the waste to be emitted into the atmosphere, the following three elementary processes must occur:

(1) The hazardous compound in the surface impoundment must travel to the surface where it is in contact with the atmosphere.

(2) At the surface (or liquid-air interface), the hazardous compound must vaporize or establish the vapor liquid equilibrium which determines its concentration in the air phase in the immediate vicinity of the surface based on the concentration in the liquid phase at the surface.

(3) Once vaporized at the interface, the hazardous component must be transported into the bulk of the air stream.

In the transport of the hazardous component in the liquid and air phases corresponding to steps 1 and 3 above, it encounters inherent resistances. If a pure volatile liquid is vaporized into the atmosphere, the resistance for steps 1 and 2 is zero, and only the resistance in the air phase (step 3) is controlling.

On the assumption of no resistance for mass transfer rate in step 2, the science of "thermodynamics" can be used to quantify the equilibrium phenomena. The mass transfer coefficients (k_L, k_g) expressed in a unit of gr-mol/cm$^{2}\cdot$ sec can also be expressed in units of #-mol/ft$^{2}\cdot$ hr, cm/sec, or 1/day. The method of conversion is shown in the examples in Section VI. The reciprocals of the resistances encountered in steps 1 and 3, or mass coefficients are designated by

k_L : liquid phase mass transfer coefficient (step 1 above), gr-mol/cm$^{2}\cdot$ sec.

k_g : gas phase mass transfer coefficient (step 3 above), gr-mol/cm$^{2}\cdot$ sec.

In addition to the volatilization of the hazardous component, other processes would occur simultaneously in the surface impoundment. Engineers are often concerned with biodegradation, transport through soil, outflow in the effluent and sludge, and accumulation. Quantitatively, one can write the following material balance for the amount of a hazardous substance being transported and transformed:

Input = Output* + Biodegradation + Air Emissions + Transport through Soil + Accumulation

Our primary concern is the air emissions. The rate of air emissions of a hazardous substance, i, is expressed by **

---

* Output includes the amount in the effluent and sludge

** The correct formula is $Q_i - Y_i\ (Q_i + Q_j) = K_Li\ Ac\ (x_i - x_i^*)$ where Y_i is the mole fraction of the component i in the air phase. Since $Q_j = 0$ (subscrip j refers to air) and $(1-Y_i) \cong 1$ for low air emissions, Equation (3) results.

$$Q_i = K_{Li} \cdot A_c \; (x_i - x_i^*) \cdot MW_i \qquad (3)$$

where Q_i : rate of air emissions of component i, gr/sec.

K_{Li} : overall mass transfer coefficient of component i (expressed in the liquid phase concentration), gr-mol/cm^2· sec

A_C : area of surface impoundment, cm^2

x_i : concentration of component i in the impounded liquid, mole fraction.

x_i^* : liquid-phase concentration of component i in equilibrium with the air phase concentration of component i, mole fraction

MW_i : molecular weight of hazardous component i.

In equation (3) K_L is the reciprocal of the overall resistance attributable to the sum of individual resistances. The method of combining the individual mass transfer coefficients is well established.

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{K \cdot k_g} \qquad (4)$$

where K is the constant establishing the equilibrium between the liquid and air phases expressed by $y_i = K_i \; x_i$, and y_i is the mole fraction of component i in the air phase. There are several ways of determining the values of K_i (K-values) for use in equation (4). There is a compilation of the results of the vapor-liquid equilibrium experiments, and Henry's law constants, from Raoult's law and the activity coefficient concept. Detail methods on the evaluation of the K-values are beyond the scope of this report. For a brief summary, the reader may consult Appendix A.

It is commonly assumed that the concentration of component i in the air stream is negligible compared with that in the liquid phase, that is $x_i^* = 0$ in Equation (3). Hence an adequate expression for the emission rate from the surface impoundment is

$$Q_i = 4047 \times 10^4 \; MW_i \cdot \overline{A}_c \cdot x_i \qquad (5)$$

where $\overline{A}_c$ is the surface area of the impoundment, acres. In order to calculate the emission rates using Equation (5), the overall mass transfer coefficient must be known. The mass transfer coefficients, k_L and k_g, in the liquid and air phases are correlated and reviewed by various experimenters in academic institutions, and industries (7)(22). The results of their correlations are summarized below:

i. liquid phase mass transfer coefficients

$$k_{Li} = (3.17 \times 10^{-3} \, R_e{*}^{0.195} - 1.39 \times 10^{-3}) \frac{\rho_M}{MW_M} \, \frac{D_{i,j}}{D_{Tol,H_2O}} \text{ by Cohen (4)} \qquad (6)$$

or

$$k_{Li} = 0.0076 \, \frac{\rho_M (1.024)^{\theta-20}}{MW_M} \, U_o^{0.67} \cdot H_o^{-.85} \, \frac{D_{i,j}}{D_{O_2,\,H_2O}}, \text{ by Owens (13)} \qquad (7)$$

where Re* is the roughness Reynolds number which can be calculated by (4)

$$Re^* = \frac{7.07 \; U_{10}^{\;1.25}}{\nu_a \; e^{\frac{56.6}{U_{10}^{0.25}}}}$$

U_{10} is the wind velocity at the height of 10 m, cm/sec, ν_a is the air kinematic viscosity, cm^2/sec, Di,j is the diffusivity of chemical i in solvent j, $D_{Tol,\,H_2O}$ is the diffusivity of toluene in water, θ is the temperature in the surface impoundment, °C; U_o is the surface velocity, ft/sec (see "NOMENCLATURE" for estimating methods) H_o is the effective depth of surface impoundment, ft, Do_2, H_2O is the diffusivity of oxygen in water, MW_M is the molecular weight of waste mixture, ρ_M is the density of the mixture, $\frac{gr}{cm^3}$, and K_{Li} is expressed in gr-mol/c^2 sec. As a footnote, in the original paper by Cohen, K_{Li} was given in cm/hr with the coefficients 11.4 and 5 in place of 3.17×10^{-3}, and 1.39×10^{-3}, respectively. The correlation is modified to convert the unit of k_{Li} from cm/hr to gr-mol/$cm^2\cdot$ sec, and to accommodate the liquid waste mixtures other than aqueous solutions. Also in the original correlation by Owens, the unit of the k_{Li} is expressed in cm/hr. In the process of converting the unit of k_{Li} to gr-mol/$cm^2\cdot$ sec, the density (ρ_M) and molecular weight (MW_M) of the mixture are incorporated in the correlation to extend its applicability to mixtures other than aqueous solutions.

ii. gas-phase mass transfer coefficients

$$k_{gi} = 1.3 \times 10^{-5} \; U_{air}^{0.78} \; N_{SC}^{-0.67} \; de^{-0.11} \; \frac{\rho_{air}}{MW_{air}} \tag{8}$$

where k_{gi} is given in gr-mol/cm^2 sec, U_{air} is wind speed in m/hr, N_{sc} is the gas Schmidt number (see "Nomenclature" for dimensional parameters), de is the effective diameter of quiscent area of surface impoundment, m, which, for aerated surface impoundments, can be calculated by substracting the effective area of aeration for mass transfer from the total surface area of basin, ρ_{air} is the density of air in #/ft^3, and MW_{air} is the molecular weight of air.

2. Aerated Surface Impoundments

a. Summary of Estimating Equations

$$Q_i = 4047 \times 10^4 \cdot MW_i \; K_{Li} \cdot \bar{A} \cdot x_i \qquad (9)$$

where the overall mass transfer coefficient should be calculated using

$$K_{Li} = (K_{Li})_c \frac{\bar{A}_c}{\bar{A}} + (K_{Li})_T \frac{\bar{A}_T}{\bar{A}} \qquad (10)$$

$(K_{Li})_c$ is the overall mass transfer coefficient for the convective region $\frac{\text{gr-mol}}{\text{cm}^2\text{, sec}}$, which can be estimated from Equation (6),(7) and (4) as explained earlier, $\bar{A}_c$ is the effective surface area of the convective region, acres, $(K_{Li})_T$ is the overall mass transfer coefficient for the turbulent region, gr-mol/cm^2· sec, the individual mass transfer coefficients of which can be estimated from Equations (11) and (12) as presented later, $\bar{A}_T$ is the effective surface area of the turbulent region, acres, $\bar{A}$ is the total surface area of the aerated surface impoundments, acres, x_i is the mole fraction of component i in the liquid mixture, and Q_i is the emission rate gr/sec.

b. Description

An aerated surface impoundment can be visualized as consisting of two zones where emissions occur. Beyond a certain region of turbulence caused by aeration, the turbulence diminishes. The air emissions are comparable to the impoundment retaining the mass transfer surface caused by natural phenomena such as wind. This will be referred to as surface impoundment retaining natural surface. The mass transfer coefficients for the zone of natural surface can be calculated by Equations (6) and (8). The second zone of concern is the core of aeration where the mass transfer coefficients are correlated from consideration of turbulence.

The correlations taken from the literature are as follows:

i. Liquid-phase mass transfer coefficients for mechanical surface aerators .

$$k_{Li}\, a_V\, V = \frac{J\ (POWR)\ (1.024)^{\theta-20}\ (\alpha)\ (10^6)}{1.31 \times 10^7} \sqrt{\frac{D_{i,H_2O}}{D_{O_2,H_2O}}}$$

by Thibodeaux (16) (11)

where k_{Li} is the liquid phase mass transfer coefficient of component i, gr-mol/$cm^2\cdot$ sec, a_v is the surface area per unit volume of surface impoundment, m^2/m^3 equal to (depth^{-1}, or m^{-1}, for a flat bottom basin), V is the volume of surface impoundment in the region of effect of aeration, J is the oxygen transfer rating of surface aerator, normally about 3 lb O_2/hr-hp, PCWR is the total power input to aerators in the aerated surface impoundment, H_p, and α is the oxygen transfer correction factor (normally has a value of around 0.8 (22)). In Equation (11), the coefficient in the original correlation is modified to convert the unit from the British to metric system.

ii. Gas-phase mass transfer coefficients

$$k_{gi} = 0.00039 \frac{\rho_g\, D_{i,air}}{d\ MW_i} (N_{Re})^{1.42} (N_{FR})^{-0.21} (N_p)^{0.4} (N_{SC})^{0.5}$$

by Reinhart (14) (12)

where k_{gi} is the gas phase mass transfer coefficient, gr-mol/$cm^2\cdot$ sec, ρ_g is the bulk phase density of gas, gr/cm^3, Di,air is the diffusivity of component i in air, cm^2/sec, d is the impeller diameter, cm, MW_i is the molecular weight of component i, and

N_{Re}, N_{FR}, N_p and N_{sc} is the Reynolds, Froude, Power and Schmidt numbers respectively. The definition of the dimensionless groups in terms of dimensional parameters can be found in the "Nomenclature."

It can be shown that the use of the area-averaged overall mass transfer coefficients in Equation (9) gives the emission rate identical to the summation of the results calculated from each zone of mass transfer in the aerated surface impoundment.

$$K_L = (K_L)_C \frac{A_C}{A} + (K_L)_T \frac{A_T}{A} \qquad (13)$$

In Equation (13) K_L is the area-averaged overall mass transfer coefficient to be used in Equation (9) for the aerated surface impoundment, $(K_L)_C$ is the overall mass transfer for the convective region, $(K_L)_T$ is the overall mass transfer coefficient for the turbulent region, A_C is the effective surface area of the convective region, A_T is the effective surface area of the turbulent region, and A is the total surface area of the aerated surface impoundment. A_C/A and A_T/A represent the fraction of the convective and turbulent surface areas, respectively.

3. Activated Sludge Processes

When a new biological treatment facility is planned, the concentration of the waste to be disposed of in the surface impoundment is normally known. The steady state concentration in the lagoon cannot be measured until actual operation. The compounds will be treated by biological oxidation, and at the same time, will be air-stripped into the atmosphere. Some of them may be adsorbed on sludge.

In this case, the concentration in the surface impoundment at the steady state condition must be estimated before the air emission rate can be estimated. Once the concentration in the lagoon is

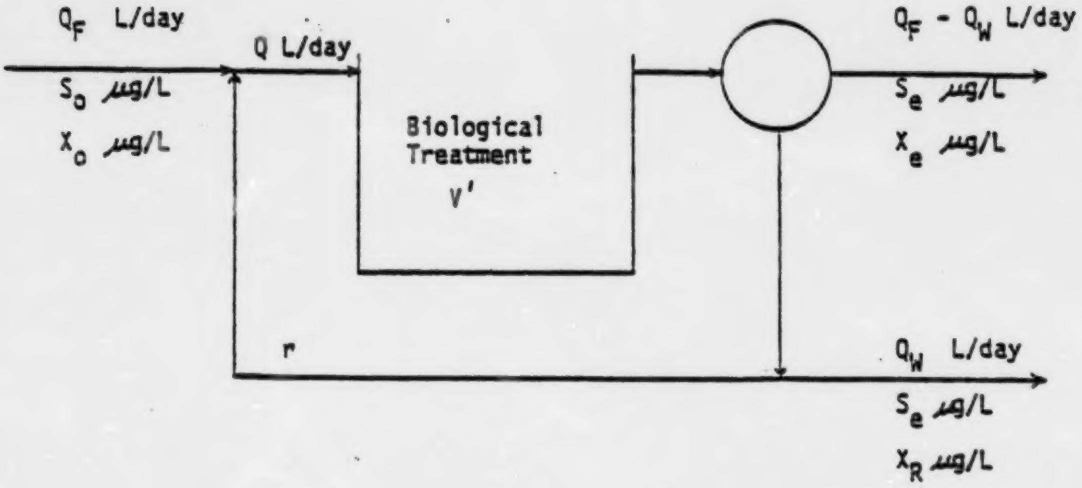
Q_F L/day
S_0 µg/L
X_0 µg/L
Q L/day
Biological Treatment
V'
$Q_F - Q_W$ L/day
S_e µg/L
X_e µg/L
r
Q_W L/day
S_e µg/L
X_R µg/L

Figure 1. A schematic of activated sludge process.

S_0 : substrate concentration in influent, µg/L

S_e : substrate concentration in effluent, µg/L

X_0, X_e, X_R : concentration of substrate on sludge in influent, effluent, and return sludge, respectively, µg/L

V': bioreactor volume, L

r : recycle ratio, volume flow rate recycle/volume flow rate feed

Q : flow rate to biological treatment ($=(1+r)Q_F$), L/day

20<

estimated, the preceding procedure can be used for estimation of air emission rates. The methodology for estimating the concentration in the commonly encountered biological unit is presented below. The detail explanation of the method can be found in References 30 and 31. Figure 1 is a schematic of a continuous activated sludge process showing the biological aerator and the sludge return and wastage. The dynamics of removal of a substrate in the biological system can be represented by writing a substrate material balance around the system as a sum of the processes contributed by the multimedia mechanisms of biodegradation, air stripping, and adsorption on sludge.

$$\begin{array}{c}\text{Input in}\\ \text{influent liquid}\end{array} + \begin{array}{c}\text{Input in}\\ \text{influent sludge}\end{array} - \begin{array}{c}\text{Output in}\\ \text{effluent liquid}\end{array} - \begin{array}{c}\text{Output in}\\ \text{effluent sludge}\end{array}$$

$$= \begin{array}{c}\text{disappearance by}\\ \text{biodegradation}\end{array} + \begin{array}{c}\text{disappearance by}\\ \text{air stripping}\end{array} + \begin{array}{c}\text{Output in}\\ \text{waste sludge}\end{array}$$

$$Q_F S_o - (Q_F - Q_W) S_e = \frac{k_{1(s)} X S_e}{S_0} V + k_a S_e V + Q_W \frac{k_1 X' S_e}{1 + K_T S_r + K_1 S_e}$$

or

$$\frac{Q_F}{Q} S_o - \left(\frac{Q_F}{Q} - \frac{Q_W}{Q}\right) S_e = \frac{k_{1(s)} X S_e}{S_0} t_c + ka S_e t_c + \frac{k_1 X' S_e}{1 + K_T S_r + K_1 S_e} \frac{Q_W}{Q} \qquad (14)$$

where t_c is the hydraulic residence time, day, X is the sludge concentration in the reactor, $\mu g/L$, X' is the maximum concentration of a substrate on sludge, $\mu g/L$, $k_{1(s)}$ is the rate constant in Grau equation (n=1), 1/day, S_o is the initial substrate concentration, $\mu g/L$, k_a is the area-averaged overall air stripping rate constant, 1/day (Note that k_L in Equation (13) can be converted to k_a by

$$k_L \left(\frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}\right) \cdot MW \left(\frac{\text{gr}}{\text{gr-mol}}\right) \frac{1}{\bar{\rho}} \frac{\text{cm}^3}{\text{gr}} \cdot \frac{1}{\text{depth (cm)}} \times 86,400 = k_a \text{ (1/day)} ,$$

S_r is the concentration of total substrates minus substrate S_e under consideration, $\mu g/L$ K_1 and K_T (use 2.4×10^{-3} L/ug) are adsorption constants (31), and X' is the maximum amount of the substrate adsorbed on sludge, $\mu g/L$.

Using the relationship $Q_F = \frac{Q}{1 + r}$, one gets

$$S_o - (1-W)S_e = \frac{k_1 X S_e}{S_o}(1+r)t_c + k_a S_e(1+r)t_c + W \frac{K_1 X' S_e}{1 + K_T S_r + K_1 S_e} \qquad (15)$$

where $W=Q_W/Q_F$ (waste sludge flow/fresh feed flow). Since the W term is small compared with 1 (numerical values to be presented later).

$$(S_o - S_e) = \frac{k_{1(s)} X S_e}{S_o}(1+r)t_c + k_a(1+r)S_e t_c + W \frac{K_1 X' S_e}{1 + K_T S_r + K_1 S_e} \qquad (16)$$

Upon rearrangement

$$S_e = \frac{-b + \sqrt{b^2 + 4 a S_o(1 + K_T S_r)}}{2 a} \qquad (17)$$

where

$$b = 1 - K_1 S_o + K_T S_r + \frac{k_{1(s)} X}{S_o}(1+r)t_c(1+K_T S_r) + k_a(1+r)t_c(1+K_T S_r) + K_1 X' W \qquad (18)$$

$$a = K_1(1 + (1+r) \frac{k_{1(s)} X}{S_o} t_c + (1+r) k_a t_c) \qquad (19)$$

Despite the presence of some volatile organic compounds in the influent, their concentrations in the wastage sludge may be below their detection limits indicating negligible adsorption on sludge. In this case, Equation (16) reduces to

$$S_e = \frac{S_o}{1 + \frac{k_{1(s)} X}{S_o}(1+r) t_c + (1+r)k_a t_c} \qquad (20)$$

The example calculations for using Equations (16) and (20), and for subsequently estimating the emission rate in the biological system is presented later. Appendix E tabulates rate constants needed in the calculations.

4. Certain Simplification of Correlations of Mass Transfer Coefficients

Repeated use of Equations (6), (8), (11), and (12) for estimting mass transfer coefficients would be cumbersome and time-consuming. Certain simplifications would facilitate estimation of these coefficients if the conditions assumed in the simplification do not substantially deviate from actual conditions.

The applicability of the correlations for the mass transfer coefficients can be extended to a non-wastewater mixture. When the air emissions from a surface impoundment treating, storing, or disposing of organic mixtures need to be estimated, the ratio of diffusion coefficient in water in Equaiton (11) should be replaced by the diffusion coefficient in the solvent to calculate the liquid-phase mass transfer coefficients. Other investigators recommend the use of the relationship (15)(18),

$$\frac{D_i \text{ in a solvent}}{D_j \text{ in a solvent}} = \left(\frac{MW_j}{MW_i} \right)^{0.5} \qquad (21)$$

The similar relationship has been used for the approximation of the gas-phase diffusivity ratios. Kyosai compares the experimental results with the ratios of molar or critical volumes in relationship to the diffusivity equation proposed by Wilke and Chang (24).

The emission rates of volatiles from the surface impoundment could be seasonal due to the seasonal temperature variation. The correction to the temperature variation can be incorporated in the evaluation of the mass transfer coefficients by recognizing the factors dependent upon the temperature. There are explicit terms for the temperature correction in the correlations of the mass transfer coefficients. The dependence of the diffusion coefficients upon temperature can be accounted for by noting that the gas phase diffusivity is proportional to temperature by 1.5 power and the liquid phase diffusivity is directly proportional to temperature, as suggested by the following equations:

Calculation of gas diffisuivity (34)

$$(D_{i,j})_G = \frac{0.0043\ T^{1.5}}{P(V_i^{1/3} + V_j^{1/3})^2} (1/MW_i + 1/MW_j)^{0.5} \qquad (22)$$

where $(D_{ij})_G$ is the diffusivity of i in j, cm^2/sec, T is the absolute temperature, °k, P the total pressure, atm, V the molecular volume, i.e., th specific molar volume of the liquid at its boiling point, cm^3/gr mol, MW the molecular weight, and subscripts i, j refer to component i and j respectively.

Calculation of liquid diffisuivity (24)

$$(D_{i,j})_L = \frac{7.48 \times 10^{-8}\ (\phi\ MW_j)^{0.5}\ T}{\mu'\ v_i^{0.6}} \qquad (23)$$

where $(D_{ij})_L$ is the diffusivity of i in dilute solution in solvent j, cm^2/sec, T the temperature, $^o k$, μ' the solution viscosity, cp, v_i the solute molal volume at the normal boiling point, cm^3/gr mol, (75.6 for the water as solute), and ϕ the association factor for solvent, (2.6 for water, 1.9 for methanol, 1 for unassociated solvents such as benzene and ethyl ether).

For a given surface impoundment, the individual mass-transfer coefficients for various compounds can be simplified by referring

σ_z - Since D stability is by far the most frequently occurring stability class, σ_z should be taken from the curve for D stability as given in Figure 2 (taken from refernce 19). The distance used to determine σ_z should be the distance from facility center to recepter (i.e., L, not L_v), becasue σ_z at the facility is assumed to be negligible.

u - Various references (e.g., the climatic Atlas of the United States (3)) provide information on annual average wind speed. If these references or this data are not available, a default value of 5 m/sec may be used.

ø - The Climatic Atlas of U.S. also compiles the frequency that the wind blows from various directions for many U.S. cities. For this screening technique, ø should be set equal to the frequency of the most common of the standard 16 wind directions. If this information is not available, a default frequency of .15 may be used.

As discussed above, the screening technique is not always suitable for estimating the impact of a disposal facility. In particular, if the source width is greater than 40% of the distance from source center to recepter, the consideration of just one sector and the use of the virtual point source approach lead to increasingly less reliable concentration estimates.

If the screening technique is not suitable, or if the screening technique implies that unacceptable impacts may occur, the Climatological Dispersion Model should be used to obtain a more accurate estimate of concentrations. This model considers average emission rates, and the joint frequency distribution of wind speed and stability class of each of 16 wind directions. (This data is generally available from the National Climatic Center in Ashville, North Carolina.) This model also provides a more sophisticated integration of the impact of area sources. This model is a computerized model available on EPA's UNAMAP system. The model is described in Reference 1. Guidance on model inputs and other issues as given in the Guideline for Air Quality Model (20) should be followed in performing this modeling.

For acutely toxic pollutants assessment of short-term effects can be accomplished by using short-term air pollution dispersion analysis for ground level concentration effects. The prediction of the worst case conditions can be performed similarly.

III. AMBIENT AIR QUALITY MODELING FOR AREA SOURCES (5)

Hazardous substances evaporated into the atmosphere from disposal facilities may introduce significant impacts on human health and the environment in the surrounding region. We will consider the use of air quality modeling to assess whether emission reductions are necessary to avoid exceeding acceptable levels of hazardous substances.

Once a maximum acceptable concentration for a hazardous substance is designated, air quality modeling can be used to estimate a maximum allowable emission rate. For modeling purposes, disposal facilities can be considered as area sources with emissions occurring at ground level. In most cases it can be assumed that no plume rise will occur. Since the health effects being considered are thought to be related to long-term exposure, the modeling techniques recommended calculate annual average concentration estimates. The highest concentration caused by a ground-level source occurs near the source. However, it is not possible to estimate concentrations closer than 100 meters from a source using standard dispersion models. Therefore, the modeling for this regulation should focus on concentrations at 100 meters from the facility or, if the property line is greater than 100 meters from the facility, at the property line.

Two approaches are possible for estimating impacts of disposal facilities. The first approach is a screening technique, i.e., a simple approach suitable for making preliminary concentration estimates. The second approach is to use a refined model, i.e., a computer program for making reasonably accurate concentration estimates. It is not always possible to use the screening technique, in which case it is necessary to use the refined model at the outset. Also, if the screening technique suggests that the facility may have an unacceptable impact, the refined model should be used to estimate the impact more accurately.

The screening technique is based on treating the disposal facility as a virtual point source. Disposal facilities have their emissions initially spread over the area of the facility. The virtual source approach hypothesizes a point source located at an appropriate distance upwind such that the horizontal dispersion at the facility is equal to the facility width. The horizontal dispersion downwind of the facility can then be simulated as if all the facility emission were being emitted from the virtual point source.

The calculation of the impact of a disposal facility is simplified by using the virtual source approximation. Further simplification is possible by assuming that the facility is a ground-level source, assuming no atmospheric destruction or decay, and using one assumed meteorological situation. Starting, for example, with the equation underlying the Climatological Dispersion Model (2), the equation simplifies to:

$$\chi = \frac{16.2\,Q}{2\pi\, L_v \sqrt{2\pi}\, \sigma_z\, u} \qquad (45)$$

where χ = net concentration (gr/m^3)

Q = emission rate (g/sec)

L_v = virtual downwind distance to receptor

σ_z = vertical dispersion coefficient (m) (given in Figure 2 as a function of downwind distance)

u = wind speed (m/sec)

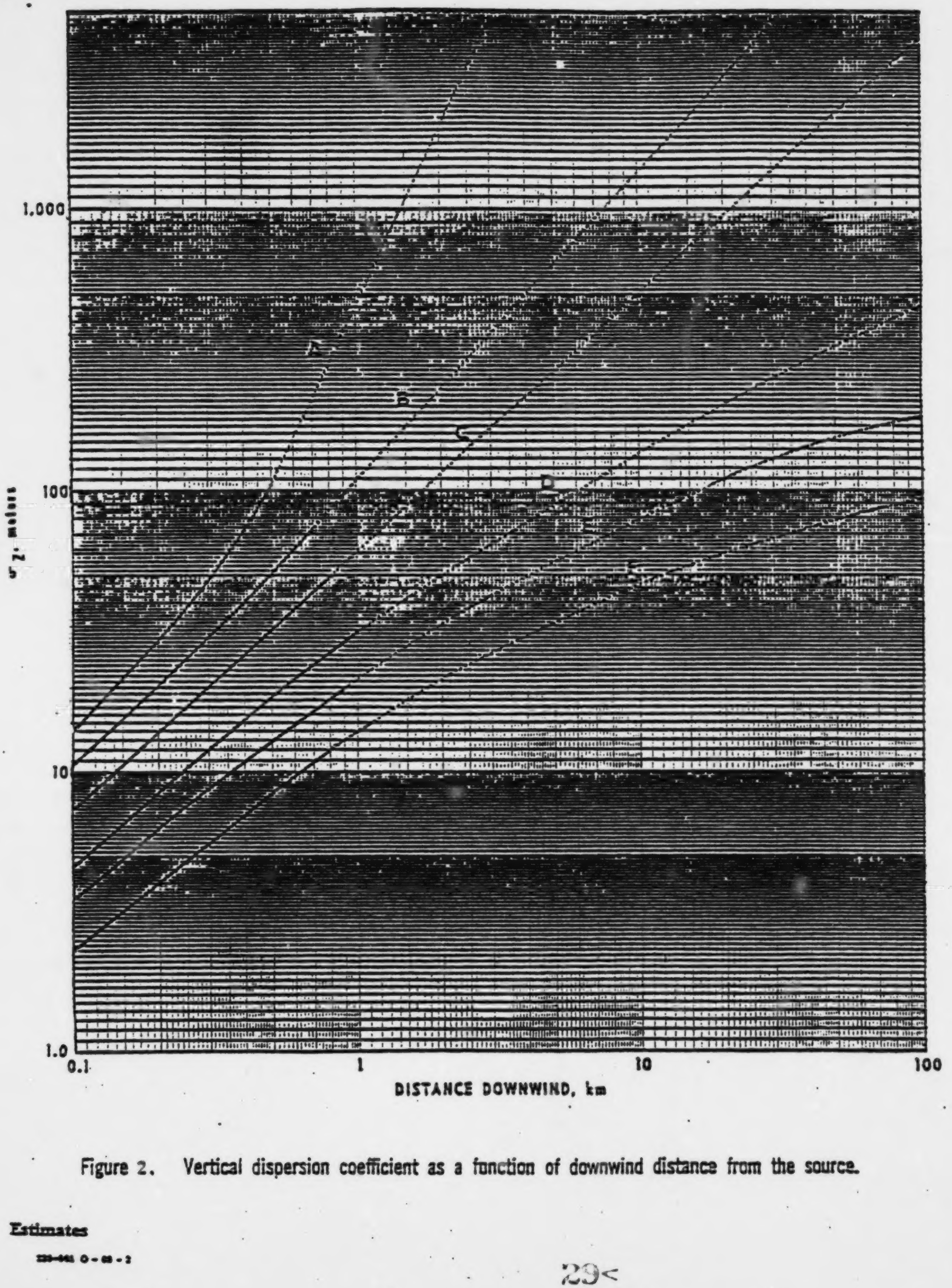

Figure 2. Vertical dispersion coefficient as a function of downwind distance from the source.

Estimates

In order to estimate the annual average concentration at a given receptor it is necessary to multiply this concentration by the frequency with which the given meteorological conditions occur. For the wind sector(s) in which the source impinges the receptor, refined models perform a summation of the concentration for each stability class and wind speed class times the frequency with which those conditions occur. The screening technique uses just one stability class and one wind speed to represent average conditions. The screening technique is limited to cases where the source emissions impinge the receptor in only one wind sector, i.e., the source lies entirely within one sector upwind. Since each sector is 22-1/2°, the source must be no more than 2L tan $\left(\frac{22 - 1/2^\circ}{2}\right)$. Thus, for a source to receptor distance (L) of 100 m, screening technique should only be used if the source is less than 40 meters in width.

If the source is adequately small compared to the source-receptor distance, the screening technique can be used by using as a frequency factor the total frequency that wind is in the sector of interest without regard to speed or stability class. The equation for calculating concentrations then becomes:

$$\chi = \left(\frac{16 \cdot 2\ Q}{2\pi\ L_v\ \sqrt{2\pi}\ \sigma_z\ u} \right) \phi \tag{46}$$

Where ϕ = frequency that wind blows from the sector of interest and other terms as defined above.

The following are recommendations for determining values for each of the parameters in the concentration equation:

χ - This is the net concentration resulting from uncontrolled emissions and is to be compared to the acceptable concentration. The concentration is proportional to the emission rate. Therefore, if the estimated concentration is a given factor higher than the acceptable concentration, then the acceptable emissions rate can be found by reducing the initially used emission rate by that factor.

Q - Earlier discussion in the document discusses the calculation of the emissions rate. Note that this is a total emissions rate for the entire area of the facility, gr./sec.

L_v - The determination of the downwind distance is complicated by the virtual source approach used in the screening technique. Let L be defined as the distance from the center of the facility to the receptor. As discussed above, L should be the greater of (1) the distance from facility center to property line, and (2) 100 meters. (Concentrations cannot be estimated less than 100 meters from a source.) The virtual point source approach also requires determining how far upwind a point source would have to be located to have the same horizontal dispersion as is inherent in the area source. This distance from the virtual point to the center of a disposal facility (L') may be calculated here as:

$$L' = \frac{S}{2} \cot \left(\frac{22\text{-}1/2^\circ}{2}\right) \qquad (47)$$

where S = the width of the facility perpendicular to the most frequent wind direction, m.

The distance to be used in calculation concentrations is the total distance from virtual point to receptor, i.e., $L_v = L + L'$.

	Calif.		N. Y.		Calif	N. J.	[illegible]			
	Ranges	Av.	Ranges	Av.	Av.			Ranges	Av.	Av.
Chemical										
Manganese										
Methyl Chloroform										
Methylene Chloride	0.6 ~12	3.8						0.01 ~12	0.05	0.035
Methyl Iodide										
Nickel									(0.009)	(0.002)
Nitrobenzene										
N-nitroso-N-ethylurea (NEU)										
N-nitroso N-methylurea (NRU)										
Perchloroethylene								0.001 ~10		0.009
Phosgene										
Polycyclic Organic Matter										
Propylene Oxide										

Chemical	Los Angeles Calif. Ranges	Los Angeles Calif. Av.	New York N. Y. Ranges	New York N. Y. Av.	Azusa Calif Av.	Bayonne N. J. Range	Near Gas Station	Urban Range	Urban Av.	Rural or Background Av.
Toluene	~ $125^{(1)}$	$37^{(1)}$			$14^{(1)}$					
Trichloroethylene										
Vinyl Chloride										
Vinylidene Chloride										
o-Xylene	$33^{(1)}$	$8^{(1)}$			$3^{(1)}$					
m-Xylene	$61^{(1)}$	$16^{(1)}$			$5.5^{(1)}$					
p-Xylene	$25^{(1)}$	$6^{(1)}$			$2^{(1)}$					
Hexachlorobenzene										
Chloroform						(0.49)~ $(73)^{(6)}$				$(0.49)^{(6)}$
PAH									$(0.0436)^{(6)}$	
Toxaphene								0 ~ $(1.54)^{(6)}$	$(0.02)^{(6)}$	(0.00053)(6
TCDD										
Carbon Tet.						0.12 ~ 18.6				0.13

Table 4. Comparison of Ambient Air Concentrations and Maximum Allowable Concentrations @ 10 Risk

Chemical	Unit Risk	Concentration @ 10^{-5} Risk $\mu gr/m^3$	 ppb	Ambient Air Conc. (ppb) Urban Av.	 Rural or Background
Acetaldehyde					
Acrolein				7.9	
Acrylonitrile	$8.5x10^{-5}$	0.1176	0.054		
Allyl Chloride	$9.9x10^{-7}$	10.1	3.23		
Arsenic	$3.4x10^{-3}$	$2.94x10^{-3}$	---	(3000)	(400)
Asbestos					
Benzene	$4.8x10^{-5}$	0.208	0.065	3 - 15	0.017
Benzyl Chloride					
Beryllium	$2.7x10^{-1}$	$3.7x10^{-5}$	---	(0.0015)	$(1.3x10^{-4})$
Cadmium	$2x10^{-3}$	$5x10^{-3}$	---	(0.001) ~(0.03)	0 ~ (0.0001)
Chlorobenzene					
Coke Ovens					

Concentration in ( ) is $\mu gr/m^3$

	Unit Risk	Concentration @ 10^{-5} Risk		Ambient Air Concentration	
		µgr/m^3	ppb	Urban Av.	Rural or Background
Chemical					
o-Cresol					
m-Cresol					
p-Cresol					
o-Dichlorobenzene					
p-Dichlorobenzene					
Diethyl-nitrosamine (DEN)	7.2×10^{-2}	1.39×10^{-4}	3.3×10^{-5}	~0	
Dimethyl-nitrosamine (DMN)	0.29×10^{-2}	3.45×10^{-3}	1.14×10^{-3}	(0.1)~ (36)	1×10^{-3}
Ethylene Dibromide	5.9×10^{-4}	1.7×10^{-2}	2.2×10^{-3}		
Ethylene Dichloride	1.2×10^{-5}	0.83	0.206		
Ethylene Oxide	1.2×10^{-4}	8.3×10^{-2}	0.046		
Formaldehyde	3.4×10^{-5}	0.294	0.24		
Maleic Anhydride					

	Unit Risk	Concentration @ 10 Risk		Ambient Air Concen	
		μgr/m^3	ppb	Urban Av.	Rural or Backgroun
Chemical					
Manganese		2.08×10^{-2}			
Methyl Chloroform					
Methylene Chloride				0.05	0.035
Methyl Iodide					
Nickel	1.8×10^{-3}	5.56×10^{-3}		(9×10^{-3})	(2×10^{-3})
Nitrobenzene					
N-nitroso-N-ethylurea (NEU)	0.65×10^{-2}	1.54×10^{-3}	3.2×10^{-4}		
N-nitroso N-methylurea (NMU)	3.5×10^{-2}	2.86×10^{-4}	6.78×10^{-5}		
Perchloroethylene	7.6×10^{-6}	1.32	0.194	0.001. ~10	0.009
Phosgene					
Polycyclic Organic Matter					
Propylene Oxide					

Chemical	Unit Risk	Concentration @ 10^{-5} Risk		Ambient Air Concentration	
		$\mu gr/m^3$	ppb	Urban Av.	Rural or Background
Toluene				10	
Trichloroethylene	4.2×10^{-6}	2.38	0.44		
Vinyl Chloride	4.1×10^{-6}	2.44	0.954		
Vinylidene Chloride	3.0×10^{-5}	0.33	0.082		
o-Xylene				5	
m-Xylene				10	
p-Xylene				4	
Hexachlorobenzene	4.8×10^{-4} *	2.1×10^{-2}	0.0018		
Chloroform	5.1×10^{-5} *	0.2	0.041	0.1 - 15	0.1
PAH	3.3×10^{-3} *	3.03×10^{-3}	3.7×10^{-4}	5.3×10^{-3}	
Toxaphene	3.2×10^{-4} *	3.1×10^{-2}	1.8×10^{-3}	1.18×10^{-3}	1.28×10^{-6}
TCDD		1.27×10^{-6}	1.1×10^{-7}		
Carbon Tet.	2.4x1[illegible]5 *	0.417	0.066	0.12 - 18.6	0.13
PCB	1.2×10^{-3} **	0.0084			

* From water quality criteria documents.

** Calculated from potency slope(4.34 1/mg/kg day) obtained from ingestion study.

Table 2 does not attempt to present exhaustively all carcinogenic compounds, but is merely a collection of data that the EPA's CAG has complied at the time this report is completed. It is not meant to limit control and risk assessment of hazardous air emissions only to those compounds in the list. The compounds which are missing from the list or the data of which are inadequate or incomplete will be added to the list as more data becomes available. If the results of a health effect study on another compound become available from some other source, such information could be used as a basis of evaluating the allowable exposure concentrations.

Also other effects on human health due to exposure to high ambient air concentrations of chemicals should not be neglected during the evaluation process. These effects include acute toxicity, responses to central nervous system, teratogenicity, mutagenicity, bioaccumiulation, radioactivity, nephrotoxicity, hepatotoxicity, phytotoxicity, toxicity to aquatic species, photochemical reactivity, etc. The compilation of data concerning these effects is not available at this time. An example presented later will address the technique of evaluating the health effect potential based on other criteria goals.

In the case of emissions of total hydrocarbons, a caution should be exercised in evaluating the impact of a facility located in the area where the ambient air quality of photochemical oxidants is not presently acceptable. Since most of hydrocarbons (except methane) participate in the formation of photochemical smog sooner or later depending upon its reaction rates, the prevention of further degradation of the ambient air quality of photochemical oxidants can be achieved by removal of volatile hydrocarbons to the extent possible.

Table 5 shows the upwind and downwind concentrations of several compounds in the ambient air around land disposal facilities (29). The organic species were collected on Tenax adsorbent and analyzed by GC/FID after identifying with GC/MS. Trace metals were collected on high-volume filters and analyzed from the collected particulates.

TABLE 5 CONCENTRATIONS OF SELECTED HAZARDOUS ORGANIC VAPORS FOUND IN THE AMBIENT AIR AT HAZARDOUS WASTE FACILITIES

Facility Code No.	Background Type ①	Ambient Air Concentrations, ppb																	
		n-Hexane		Benzene		n-Heptane		Toluene		n-Octane		Ethyl Benzene		Xylenes		Dichloro-Benzene		Naphthalene	
		Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind	Up-wind	Down-wind
13	R, I	15.0	11.0	4.0	5.0	42.0	2.0	58.0	60.0	6.7	2.2	4.9	11.0	10.0	32.0	0.0	1.6	0.0	0.8
14	R, I	3.4	10.0	8.4	83.0	3.0	15.0	22.0	30.0	2.3	3.8	3.0	8.8	10.0	16.0	0.0	0.0	0.2	0.0
15	R	7.4	20.0	6.1	240.0	4.4	100.0	26.0	170.0	1.4	25.0	3.4	64.0	15.0	240.0	0.3	26.0	0.5	22.0
16	R	14.0	42.0	11.0	44.0	12.0	36.0	106.0	150.0	5.0	31.0	21.0	24.0	94.0	100.0	3.0	3.0	0.0	
17	U	24.0	98.0	28.0	84.0	27.0	97.0	150.0	950.0	20.0	46.0	28.0	37.0	79.0	140.0	3.0	6.6	3.0	8.0
18	U	15.0	42.0	10.0	57.0	11.0	62.0	8.5	30.0	8.0	38.0	16.0	56.0	54.0	270.0	0.8	3.7	0.4	4.0

①Background Type: R = Rural, I = Industrial, U = Urban

Cont'd

TABLE 5 PARTICULATE TRACE METALS IN AMBIENT AIR AT HAZARDOUS WASTE FACILITIES

Facility Code No.	Back-① Ground Type	Trace Metal Concentration, µg/m³															
		Cadmium		Chromium		Cobalt		Copper		Iron		Lead		Nickel		Zinc	
		up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind	up-wind	down-wind
01	U	BDL②	BDL	0.14	0.18	BDL	BDL	0.12	0.16	3.2	5.9	0.51	0.62	BDL	0.03	0.08	0.33
04	R	BDL	BDL	.11	.12	BDL	BDL	.01	.15	.40	1.69	.06	.90	BDL	BDL	BDL	.08
05	R	BDL	BDL	BDL	BDL	BDL	BDL	BDL	.04	.36	10.7	.04	.47	.04	.05	BDL	BDL
06	R	BDL	BDL	.07	.17	.04	.04	.05	.13	4.0	30.9	.45	.80	.03	.14	.02	.46
07	U	BDL	BDL	BDL	.45	.07	.13	.06	.84	10.5	71.4	.90	2.83	.04	.35	.23	2.45
08	R	BDL	BDL	BDL	BDL	.07	.05	.05	.03	1.0	2.8	.32	.34	.05	.02	BDL	.62
09	R	BDL	BDL	BDL	BDL	BDL	BDL	.16	.20	.47	.29	.09	.09	BDL	BDL	BDL	.11
10	U	BDL	BDL	BDL	.04	BDL	BDL	.27	.27	6.0	5.9	.67	.54	BDL	BDL	.21	.46
11	U	BDL	BDL	.03	BDL	BDL	BDL	.12	.08	3.9	4.6	.35	.38	BDL	BDL	.43	.42
12	U	BDL	BDL	BDL	BDL	.01	.02	.13	.09	5.5	5.6	.41	.54	BDL	BDL	.48	.44
13	R,I	BDL	BDL	BDL	BDL	BDL	BDL	.03	.06	.53	2.7	BDL	.13	BDL	.02	.05	.10
14	R,I	BDL	BDL	BDL	BDL	BDL	BDL	.12	.02	.44	.54	.06	.13	BDL	BDL	.08	.16
15	R	BDL	BDL	BDL	BDL	BDL	BDL	.05	.01	3.4	10.2	.18	.28	.02	.12	.06	.07
16	R	BDL	.03	BDL	BDL	BDL	BDL	.02	.03	.70	.07	.02	.06	.01	BDL	.02	.04
17	U	.03	.04	.02	.08	BDL	BDL	.28	.17	5.2	21.1	.91	1.23	.05	.09	.28	.70
18	U	BDL	.03	BDL	.12	BDL	BDL	.11	.19	3.9	28.8	.42	2.19	.02	.11	.03	1.53
DL③, µg/m³		.02		.01		.01		.01		.02		.01		.02		.01	

① Background type: R = Rural, U = Urban, I = Industrial

② BDL = Below detection limit

③ DL = Detection Limit

IV. EVALUATION OF EXPOSURE CONCENTRATION

The subject of risk assessment is beyond the scope of this manual. The presentation in this Chapter will focus on aspects of evaluation pertinent to arriving at acceptable ambient levels of hazardous substances. It is neither attempted to recommend a risk level or to present an exhaustive list of chemicals exhibiting evidence of carcinogenesis or other health effects.

Hazardous materials volatilized from surface impoundments, landfills, and land treatment facilities will be dispersed into the atmosphere by wind and will impact the downwind population. The maximum allowable concentration represents the level that may result in incremental risk of human health over the short-term or long-term period at an assumed risk. For carcinogenic compounds for example, the long-term effect will be cancer risk over the lifetime. If one defines the unit risk for a carcinogenic compound (Ru) as lifetime risk if the concentration of a hazardous substance in the air is 1 $\mu gr/m^3$ and if this is breathed continuously for a lifetime, the maximum allowable concentration, C_{mi} ($\mu gr/m^3$), at a tolerable level of risk can be obtained by

$$c_{mi} = risk/Ru \tag{67}$$

The unit risk for a number of hazardous compounds obtained from the EPA's Cancer Assessment Group is listed in Table 2 (12).

The background ambient concentration will indicate the present level of concentration at a locality which becomes additive to the long-term or short-term effect on the downwind impact. In order to study the level of present ambient air risk for various toxic compounds,

Chemical	Date	Excellent	Substantial	Suggestive	Inadequate Data	Unit Risk
Acetaldehyde	1/80			X		—
Acrolein	2/80			X		—
Acrylonitrile	4/78	X				8.5×10^{-5}
Allyl Chloride	9/79			X		9.9×10^{-7}
Arsenic	4/78	X				3.4×10^{-3}
Asbestos	6/78	X				—
Benzene	1/79	X				4.8×10^{-5}
Benzyl Chloride	8/79				X	—
Beryllium	12/79		X			2.7×10^{-1}
Cadmium	5/76		X			2×10^{-3}
Chlorobenzene	9/79				X	—
Coke Ovens	3/78	X				—

Chemical	Date	Excellent	Substantial	Suggestive	Inadequate Data	Unit Risk
o-Cresol	6/79				X	——
m-Cresol	6/79				X	——
p-Cresol	6/79				X	——
o-Dichlorobenzene	9/79			X		——
p-Dichlorobenzene	9/79		X			7.2×10^{-2}
Diethyl-nitrosamine (DEN)	12/79		X			0.29×10^{-2}
Dimethyl-nitrosamine (DMN)	12/79		X			5.9×10^{-4}
Ethylene Dibromide	4/78		X			1.2×10^{-5}
Ethylene Dichloride	6/78		X			1.2×10^{-4}
Ethylene Oxide	10/79		X			1.4×10^{-5}
Formaldehyde	11/79				X	——
Maleic Anhydride	2/79					

Weight of Carcinogenic

Chemical	Date	Excellent	Substantial	Suggestive	Inadequate Data	Unit Risk
Manganese	8/79			X		4.8×10^{-4}
Methyl Chloroform	1/79			X		——
Methylene Chloride	1/79			X		——
Methyl Iodide	9/79			X		——
Nickel	12/79	X				1.8×10^{-3}
Nitrobenzene	6/79				X	——
N-nitroso-N-ethylurea (NEU)	12/79		X			$.65 \times 10^{-2}$
N-nitroso N-methylurea (NMU)	12/79		X			3.5×10^{-2}
Perchloroethylene	4/78		X			7.6×10^{-6}
Phosgene	8/79				X	——
Polycyclic Organic Matter	7/78	X				——
Propylene Oxide	9/79			X		——

List of Chemicals Assessed
Weight of Carcinogenic Evidence

Chemical	Date	Excellent	Substantial	Suggestive	Inadequate Data	Unit Risk
Toluene	8/79				X	——
Trichloroethylene	8/78		X			4.2×10^{-6}
Vinyl Chloride	8/78	X				4.1×10^{-6}
Vinylidene Chloride	5/78		X			3.0×10^{-5}
o-Xylene	9/79				X	——
m-Xylene	9/79				X	——
p-Xylene	9/79				X	——

POM – It should be emphasized that POM represents a mixture of organic compounds. There is substantial evidence that some components of POM particularly from combustion processes are associated with induction of human cancer. Special attention should be given to POM emission because not all the components have evidence for its carcinogenic action. So the source and composition is important in characterizing the specific POM emission.

Beryllium – The risk unit is very high and may be revised when final data are available from the Mancuso study.

Unit risks calculated from ingestion study potency slopes are tabulated in Appendix D.

urban and rural ambient data for several compounds have been gathered. Table 3 summarizes the collected data. As one might have expected, the ambient air concentrations vary from location to location.

The Water Criteria Documents (6) make use of a risk range of 10^{-5} to 10^{-7} in presenting the exposure concentration levels of carcinogens. Table 4 is a comparison of the ambient air data with the maximum allowable concentration calculated at 10^{-5} risk. The third and fourth columns in the table represent the maximum allowable concentrations at 10^{-5} risk in gr/m^3 and ppb respectively. The ambient air concentration values which are considered "representative" for background are chosen and tabulated in Columns 5 and 6 for the purpose of comparison. It can be seen that the present ambient levels of some compounds are already too high to meet the 10^{-5} risk value. In fact, in certain urban areas, the ambient air levels exceed 10^{-5} risk at present. The ambient air concentrations higher than those in Table 3 are reported in Reference (28) for several metropolitan areas in the State of California.

In an area with a higher background concentration, the emission rate allowable for a disposal facility should be comparatively less. If the ambient air concentration in an area is higher than the 10^{-5} risk level, it may not be possible to achieve the maximum allowable concentration calculated by Equation (48) at that risk. The case-by-case evaluation will determine whether or not the facility will contribute significantly to degradation of present ambient levels so as to require reduction or elimination of hazardous emissions. The permit evaluation will consider risk assessment in consistency with other criteria goals.

Chemical	Los Angeles Calif. Ranges	Los Angeles Calif. Av.	New York N. Y. Ranges	New York N. Y. Av.	Azusa Calif. Av.	Bayonne N. J. Ranges	Near Gas Station Ranges	Urban Ranges	Urban Av.	Rural or Background Av.
Acetaldehyde	highest 13.1$^{(6)}$	7.9$^{(6)}$								
Acrolein										
Acrylonitrile										
Allyl Chloride*										
Arsenic								(1000)~ (83000)$^{(6)}$	(3000)$^{(6)}$	(400)$^{(6}$
Asbestos			(0.003) ~(0.065)$^{(6)}$	(0.015)$^{(6)}$						
Benzene	~57$^{(1)}$	15$^{(1)}$					300~ 2400$^{(6)}$			0.017$^{(}$
Benzyl Chloride										
Beryllium								(0.001) ~(0.008)$^{(6)}$	(0.0015)$^{(6)}$	(0.000
Cadmium			(0.006) ~(0.007)$^{(8)}$					(0.001) ~(0.3)$^{(8)}$	(0.03)$^{(8)}$	0 ~ (0.0001)$^{(}$
Chlorobenzene										
Coke Ovens										

* Concentrations in ppb; (   ) in $\mu gr/m^3$. Superscript refers to the reference cited.

Chemical	Ranges	Av.	Background Av.
o-Cresol			
m-Cresol			
p-Cresol			
o-Dichlorobenzene			
p-Dichlorobenzene			
Diethyl-nitrosamine (DEN)			
Dimethyl-nitrosamine (DMN)	$\sim 0^{(6)}$		
Ethylene Dibromide	(0.1) ~(36)		(0.001) ~(0.04)
Ethylene Dichloride			
Ethylene Oxide			
Formaldehyde			
Maleic Anhydride			

to a typical compound whose base values are known or easy to evaluate. Several experimenters (13), (15), (16) used oxygen as reference compound for the liquid phase mass transfer, and water vapor as reference compound for the air phase mass transfer. Upon taking the ratios of Equations (6 or 7), (8), (11), and (12) with respect to a reference compound, and considering the temperature effect with respect to a reference compound and temperature (25°C used in the present example below), one can obtain simplified relationships. For example, the liquid phase mass transfer coefficient for oxygen in a given surface impoundment, k_L, , can be calculated from Equation (6).

$$k_{L,O_2} = (3.17\text{x}10^{-3}\ \text{Re}^{*0.195} - 1.39\text{x}10^{-3})\ \frac{\rho_M}{MW_M}\ \frac{D_{O_2,j}}{D_{Tol,H_2O}} \qquad (24)$$

Also for a component i in the surface impoundment, the liquid phase mass transfer coefficient is given by

$$k_{L,i} = (3.17\text{x}10^{-3}\ \text{Re}^{*0.195} - 1.39\text{x}10^{-3})\ \frac{\rho_M}{MW_M}\ \frac{D_{i,j}}{D_{Tol,H_2O}} \qquad (25)$$

Since for a surface impoundment at a given condition the roughness Reynolds number is the same in Equations (24) and (25). By proportioning these two equations, one can get

$$k_{L,i} = \frac{D_{i,j}}{D_{O_2,j}}\ k_{L,O_2} = \left(\frac{MW_{O_2}}{MW_i}\right)^{0.5}\ k_{L,O_2} \qquad (26)$$

Similar relationships can be obtained for other individual mass transfer coefficients. The results are summarized below:

1. Convective surface (or natural surface)

   a. liquid-phase

$$k_{L,i} = \left(\frac{MW_{O_2}}{MW_i}\right)^{0.5} \left(\frac{273 + \theta}{298}\right) k_{L,O_2} \qquad (27)$$

   b. gas-phase

$$k_{g,i} = \left(\frac{MW_{H_2O}}{MW_i}\right)^{0.335} \left(\frac{273 + \theta}{298}\right)^{1.005} k_{g,H_2O} \qquad (28)$$

2. Turbulent surface

   a. liquid-phase

$$k_{L,i} = \left(\frac{MW_{O_2}}{MW_i}\right)^{0.25} \left(\frac{1.024^{\theta-20}}{1.024^{5}}\right) \left(\frac{273 + \theta}{298}\right)^{0.5} k_{L,O_2} \qquad (29)$$

   b. gas-phase

$$k_{g,i} = \left(\frac{MW_{H_2O}}{MW_i}\right)^{0.25} \left(\frac{298}{273 + \theta}\right)^{0.92} k_{g,H_2O} \qquad (30)$$

The liquid phase mass transfer coefficients for oxygen and the gas-phase mass transfer coefficients for water vapor are calculated using Equations (6)(8)(11), and (12) and listed on Table 1. The convective liquid-phase mass transfer coefficients calculated by Equation (6) is 1.23×10^{-4} gr-mol/cm^2· sec in comparison with 1.28×10^{-5} gr-mol/cm^2· sec calculated by Equation 7. The former represents the results obtained from the wind tunnel experiments, and the latter is for free flowing stream. The liquid-phase and gas phase mass transfer coefficients for all substances of concern can be calculated individually by Equations (6), (8), (11), and (12), or more simply by Equations (27) through (30). The experimental and calculated mass transfer coefficients for O_2 in the liquid phase and H_2O in the air phase is needed to use Equations (27-30). The data used in calculating the mass transfer coefficients in Table 1 are summarized in Appendix C. Table 1 is for illustration purposes only. It may be necessary to calculate mass transfer coefficients for the reference compounds or for the compounds of interest to suit each application using Equations (6), (8), (11), and (12). The field measurement values in the literature are comparable to these values (15) (22).

Table 1. Mass Transfer Coefficients for Reference Compounds (25°C)

	Convective Surface	Turbulent Surface
k_L (gr-mol/cm$^2\cdot$ sec)	1.23×10^{-4}	0.13
(O_2 in water)	0.91 (lb-mol/ft$^2\cdot$hr.)	946 (lb-mol/ft$^2\cdot$hr)
k_g (gr-mol/cm$^2\cdot$sec)	5.8×10^{-5}	9.5×10^{-4}
(H_2O in air)	0.43 (lb-mol/ft$^2\cdot$hr)	7 (lb-mol/ft$^2\cdot$hr)

5. Landfills

a. Summary of Estimating Equations

$$q_i = D_i \frac{P_a^{10/3}}{P_T^2} \frac{C_i^*}{h} \tag{31}$$

or

$$q_i = D_i \frac{P_a^{10/3}}{P_T^2} \gamma_i C_{si} \frac{x_i}{h} \tag{32}$$

which for dry soil cover reduces to

$$q_i = D_i P_T^{4/3} \frac{C_i^*}{h} \tag{33}$$

or

$$q_i = D_i P_T^{4/3} \gamma_i C_{si} \frac{x_i}{h} \tag{34}$$

where q_i is the emission rate of component i per unit area, $gr/cm^2 \cdot sec$, D_i is the diffusion coefficient of component i in the gas phase, cm^2/sec, C_i^* is the concentration of component i in the air space in the immediate vicinity of the waste (or in equilibrium with the waste), gr/cm^3, P_a is the air-filled porosity, ($P_a = 1-\rho_B/2.65-w \cdot \rho_B$), ρ_B is the soil bulk density, gr/cm^3, the number 2.65 represents the true density of most mineral soil in gr/cm^3, w is the soil water content, gr/gr, P_T is the total porosity, cm^3/cm^3, ($P_T = 1 - \rho_B/2.65$), h is the depth of soil cover, cm, $_i$ is the activity coefficient of component i in the waste, and C_{si} is the saturation vapor concentration of component i, gr/cm^3, $C_{si} = P_i^o \; MW_i/RT$; P_i^o = vapor pressure of component i, mmHg, MW_i = molecular weight of component i, R = gas constant, 62,363 $cm^3 \cdot mmHg/°k \cdot mol$, T = temperature, °k), and x_i is the mole fraction of component i in the waste.

Note that Equations (31) through (34) are to be used for estimating emission rates when the gas generation in the landfill is insignificant.

b. Description.

The approach to estimation of air emissions from landfills presented here is an extension of the study on hexachlorobenzene emissions from landfills undertaken under the EPA contract (7). The estimation method described by Farmer is based on the diffusional process in the soil pore. Additional emissions of air pollutants caused by generation of gases in soil are shown by Thibodeaux (17) to be a significant portion of air emissions when the hazardous waste is landfilled with gas-generating wastes such as domestic garbage.

Farmer et al. presented a method of estimating the emission rate from landfills based on the controlling mechanism of diffusion through soil. Chemical vapors originated from hazardous waste move upward by molecular diffusion until the vapors reach the air-soil interface. The rate of air emissions at steady state is expressed by

$$q_i = - D_i \frac{P_a^{10/3}}{P_T^2} \frac{(C_{io} - C_i^*)}{h} \quad (35)$$

where q_i is the rate of emissions of component i per unit area, $gr/cm^2 \cdot sec$, D_i is the diffusion coefficient of component i in the gas phase, cm^2/sec, P_a is air-filled porosity, cm^3/cm^3, ($P_a = 1 - \rho_B/2.65 - w\ \rho_B$), ρ_B is the soil bulk density, gr/cm^3, w is the soil water content, gr/gr, P_T is the total porosity, cm^3/cm^3, ($P_T = 1 - \rho_B/2.65$), h is the depth of soil cover, cm, C_{io} is the concentration of component i at the soil-air interface, gr/cm^3, C_i^* is the concentration of component i in the air space at the immediate vicinity of the waste (or in equilibrium with the waste), gr/cm^3.

Thibodeaux presented the following simple expression to incorporate the long-term values for the site-specific soil conditions (17).

$$q_i = - K_{G,i} (C_i - C_i^*) (2.44 \times 10^4) \quad (36)$$

where 2.44×10^4 is the molar volume of gas, $cm^3/gr\text{-}mol$, $K_{G,i}$ is the overall mass transfer coefficient (expressed in the gas phase concentration), $gr\text{-}mol/cm^2 \cdot sec$, and C_i is the concentration of component i in the air far away from the soil-air interface. The overall mass transfer coefficient is expressed by

$$\frac{1}{K_{G,i}} = \frac{1}{k_{s,i}} + \frac{1}{k_{g,i}} \qquad (37)$$

where $k_{s,i}$ is the soil phase mass transfer coefficient of component i (expressed in the gas phase unit), gr-mol/cm^2·sec, or $k_{s,i} = D_i \cdot \epsilon / (h \cdot \tau \cdot 2.44 \times 10^4)$, ϵ is the porosity of the cover material, τ is the tortuosity, and $k_{g,i}$ is the air phase mass transfer coefficient, gr-mol/cm^2·sec.

It has been shown that the resistance to air emissions in the air phase is negligible compared with that in the soil phase (17). Equation (36) can be used with $C_i = 0$ for all practical purposes.

The diffusion coefficient in the gas phase is dependent upon the type of compound, and temperature, and can be related to the variation of molecular weight and temperature by the following proportionality relationship (7) (18).

$$D_i \propto \left(\frac{1}{MW_i}\right)^{0.5} (T)^{1.5} \qquad (38)$$

or

$$D_i = \left(\frac{MW_1}{MW_i}\right)^{0.5} \left(\frac{T}{T_1}\right)^{1.5} D_1 \qquad (39)$$

where MW_i is the molecular weight of component i, gr/mol, and T is temperature, °K.

Farmer (7) used the vapor pressure of component i to conservatively express the concentration of the volatilizing material in air, or

$$C_{si} = \frac{P_i^o MW_i}{RT} \qquad (40)$$

where C_{si} is the saturation vapor concentration of component i, gr/cm^3, P_i^o is the vapor pressure of component i, mmHg, MW_i is the molecular weight of component i, R is the gas constant (62,363 cm^3 mmHg/^{o}K·mol), T is temperature, °C. Since pure component vapor pressure is used in calculating the concentration of component i, Equation (40) is applicable in estimating emission rates from landfills only when pure compound is landfilled. C_{si} can be used in place of C_i^* in Equation (35).

When a mixture waste is landfilled, Equation (40) should be modified to incorporate the partial pressure of component i in the air phase, or

$$C_i^* = \frac{p_i^* MW_i}{RT} \qquad (41)$$

where p_i^* is the partial pressure of component i in equilibrium with the waste, mmHg. The partial pressure and vapor pressure are the same only when pure component is considered. The partial pressure in a liquid mixture can be estimated from a thermodynamic relationship

$$p_i^* = \gamma_i P_i^o x_i \qquad (42)$$

where γ_i is the activity coefficient of component i in the waste, and x_i is the mole fraction of component i in the waste. Substitution of Equation (42) into Equation (41) will give

$$C_i^* = \frac{\gamma_i \, P_i^o \, MW_i}{R \, T} x_i \tag{43}$$

Combining Equations (35) and (43), one gets

$$q_i = D_i \frac{P_a^{10/3}}{P_T^2} \frac{\gamma_i \, P_i^o \, MW_i \, x_i}{R \, T \quad h} \tag{44}$$

where it is assumed that C_{io} is small compared with C_i^*, or $C_{io} \cong$ o. Using the relationship given by Equation (40), or $C_{si} = P_i° \, MW_i/RT$, one can simplify Equation (44) to

$$q_i = D_i \frac{P_a^{10/3}}{P_T^2} \gamma_i \, C_{si} \frac{x_i}{h} \tag{45}$$

For dry soil cover when $P_a = P_T$, Equation (45) becomes

$$q_i = D_i \, P_T^{4/3} \, \gamma_i \, C_{si} \, \frac{x_i}{h} \tag{46}$$

The equations given by Shen in references (32) and (33) take the form similar to Equation (46), but are not consistent in that the effect of activity coefficient on volatility in the waste mixture is omitted, and the weight percent is used instead of mole fraction. The effect of activity coefficient may be important especially when leachate formation is considered in the volatilization rate.

These equations show that information needed for the estimation includes the porosity, moisture content, and bulk density of cover soil, the partial pressure of component i in equilibrium with the waste, the cover thickness, the molecular weight of the component, temperature, and the landfill area.

The solid waste landfilled with the hazardous waste is subject to the biological process occurring in soil, and generates gases due to anaerobic processes. The convection caused by the generated gases carries volatile chemicals toward the surface of soil. Thibodeaux (17) incorporated the transport mechanism to account for the air emissions resulting from the moving gas. The equation presented for the rate of air emissions is

$$q_i = \bar{V} \frac{C_i^* - C_{io}}{\exp\left(\frac{h \cdot \bar{V} \cdot \tau}{D_i \cdot \epsilon}\right) - 1} + \bar{V} C_i^* \qquad (47)$$

where $\bar{V}$ is the average gas velocity in the soil pore in the upward direction, cm/sec. In order to obtain the concentration of component i at the soil-air interface, C_{io}, the air-phase mass transfer given below by Equation (49) should be utilized,

$$q_i = -k_{g,i} \, (C_{ioo} - C_{io}) \; 2.44 \times 10^4 \qquad (48)$$

Equations (47) and (48) should be solved simultaneously to estimate the emission rates from a landfill with gas generation. Several examples of using Equations (47) and (48) are given in the example section.

The comparison between Equations (35) and (36) shows that the porosity and the air-filled porosity are related by

$$\epsilon = 1.73 \frac{P_a^{10/3}}{P_T^2} \qquad (49)$$

where the number 1.73 represents $\sqrt{\tau}$ or $\sqrt{3}$.

There are other transport processes which will add to air emissions. Several investigators are concerned with the effect of barometric pumping and thermal diffusion caused by temperature gradient across the soil. It appears that the role of these processes is insignificant compared with the overall emissions. Hence these additional emissions are not considered in this report.

Synthetic material is often used as a cover material. Farmer expresses the effectiveness of the synthetic material in retarding the volatilization and movement of chemical vapors in terms of the equivalent thickness of soil (25). He presented a graph which correlates polyethylene thickness (h_f, cm) in terms of the equivalent thickness of soil ($h_{eq.}$, cm) corresponding to a bulk density (ρ_B) of 1.19 gr/cm^3 and a soil water content (w) of 0.2 gr/gr. This correlation can be presented by the following equation:

$$h_{eq} = 134.6\ h_f \tag{50}$$

When synthetic material and soil are used together in layers, their individual resistances to air emissions are additive. Equation (35) can be rewritten as

$$q_i = D_i \left[\frac{1}{\dfrac{h}{P_a^{10/3}/P_T^2} + \dfrac{h_{eq}}{P_{al}^{10/3}/P_{Tl}^2}} \right] C_i^* \tag{51}$$

where P_{al} and P_{Tl} are the air filled porosity and the total porosity, respectively, used in obtaining the equivalent soil thickness, and it is assumed that $C_{io} = 0$. The data presented by Farmer can be used to evaluate the values of P_{al} and P_{Tl} as follows:

$$P_{Tl} = 1 - \frac{1.19}{2.65} = 0.551$$

$$P_{al} = P_{Tl} - (0.2)(1.19) = 0.313$$

Then Equation (32) becomes

$$q_i = D_i \left[\frac{1}{\dfrac{h}{P_a^{10/3}/P_T^2} + \dfrac{134.6\ h_f}{0.313^{10/3}/0.551^2}} \right] C_i^* \qquad (52\ )$$

or

$$q_i = D_i \left[\frac{1}{\dfrac{h}{P_a^{10/3}/P_T^2} + 1962.8\ h_f} \right] C_i^* \qquad (53)$$

Similarly, the estimation of air emission rates from a landfill covered by soil and polyethylene film with internal gas generation can be made by

$$q_i = \bar{V} \frac{C_i^* - C_{io}}{\exp\left[\dfrac{\bar{V}}{D_i} \left(\dfrac{h}{P_a^{10/3}/P_T^2} + 1962.8\ h_f \right) \right] - 1} + \bar{V}\, C_i^* \qquad (54)$$

6 . Land Treatment Facilities

There is very limited information with regard to models and experimental data dealing with air emissions during land treatment operations. Recent experimental results sponsored by API indicate that important variables significantly affecting air emissions include soil type, humidity, and loading rate. These experiments are carried out on a laboratory scale using oily sludges generated in refineries. Other factors under study are temperature, air velocity, and mode of application. The sludges are applied into soil by surface spreading and subsurface injection.

The rate of emissions at time t (sec.) after the application of the waste by surface spreading or subsurface injection can be expressed by*

$$q_i = \frac{D_{ei}\ C_{ig}}{\left[h_s^2 + \frac{2\ D_{ei}\ t\ A(h_p - h_s)\ C_{ig}}{m_{io}}\right]^{1/2}} \qquad (55)$$

where q_i is the rate of emission of component i, $gr/cm^2 \cdot sec$, D_{ei} is the effective diffusivity of component i in the air-filled soil pore, cm^2/sec, m_{io} is the initial amount of component i placed for land treatment, gr, h_s is the depth of subsurface injection, cm, h_p is the depth of soil contamination below the soil surface, cm (assumed to be 5 - 6 inches = 12.7 - 15.24 cm), A is the surface area of waste application, cm^2, C_{ig} is the gas-phase concentration of component i at the oil-gas interface in the soil pore, gr/cm^3.

The concentration of component i in the gas side of the interface, C_{ig}, can be determined by (See the Appendix for derivation)

$$C_{ig} = \left[\frac{H_c}{1 + H_c \frac{6\ D_{ei}\ z_o}{D_{wi}\ a_s(h_p^2 + h_p\ h_s - 2\ h_s^2)}}\right] C_{iwo} \qquad (56)$$

---

* See the appendix for detailed derivation supplied by Thibodeaux. This model has not been verified experimentally except the API's preliminary data.

where H_c is the Henry's law constant in concentration, C_{iwo} is the initial concentration of i in the oily waste, gr/cm^3, z_o is the oil layer diffusion length, cm, D_{wi} is the effective diffusivity of i in the waste, cm^2/sec, and a_s is the interfacial area per unit volume of soil, cm^2/cm^3.

The average emission rate over the evaporation life-time t_d sec can be obtained by integrating Equation (55) and dividing with respect to time, which yields

$$\overline{q}_i = 2\, q \text{ at } t = t_d \qquad (57)$$

where t_d is the dry-out time, sec, to be determined by

$$t_d = \frac{(h_p + h_s)}{2\, D_{ei}\; C_{ig}} \left(\frac{m_{io}}{A}\right) \qquad (58)$$

The path length of diffusion through the film and lump type of oil in soil can be estimated from .

$$z_o = \frac{d_p\, \bar{\rho}_p\, w_f}{6\, \bar{\rho}_w} \quad \text{for film form oil} \qquad (59)$$

$$z_o = \frac{d_p}{2} \quad \text{for lump form oil} \qquad (60)$$

Where d_p is the soil clump diameter, cm, $\bar{\rho}_p$ is the soil clump density (2.65 gr/cm^3), w_f is the fraction of oil in film form on the soil, and $\bar{\rho}_w$ is the waste oil density, gr/cm^3. The interfacial area is

$$a_s = 6/d_p \quad \text{for film} \qquad (61)$$

$$a_s = 2.7/d_p \quad \text{for lump} \qquad (62)$$

The mass fraction of oil in the film form can be estimated by

$$w_f = \frac{0.5\, M_T}{h_p\;\bar{\rho}_B\; A} \qquad (63)$$

where $\bar{\rho}_B$ is the bulk soil density, gr/cm^3, and M_T is the total application amount of waste, gr. The example calculations given later will facilitate the use of the above equations.

Volatile wastes are incorporated into soil for land treatment by subsurface injection. This method of application reduces volatilization in comparison with surface spreading, and bring the waste in intimate contact with microbia in soil. The depth of subsurface injection is 5 - 6" in the commercial practice.

V. CONTROL TECHNOLOGIES

Removal of volatiles from the waste prior to disposal will reduce their air emissions. Some suggest the use of wind barriers to slow down emission rates from surface impoundments. The techniques of removing volatile organic compounds from wastewaters have been extensively reviewed previously (1), (10). Some of the engineering principles of these techniques will be presented in the later part of this manual.

Steam stripping is one of the control alternatives for removal of volatiles from wastewater prior to surface impoundment. For hydrocarbon mixtures, control alternatives would be recycle or recovery of volatiles by conventional distillation processes, or disposal by incineration. Use of adequate cover material for landfills and adequate depth of subsurface injection for land treatment may provide some or considerable reduction in air emission.

Hazardous wastes landfilled with sanitary wastes are subject to considerable volatilization as a result of decomposition of waste material. Extraction of decomposition gas from sanitary landfills has been practiced by means of a collection system which consists of a series of gas wells operating under vacuum. The evaluation of an emission potential of such a landfill will require knowledge on the emission rate from the landfill, and the gas collection rate.

The method of evaluating steam stripping and solvent extraction is presented in Part C of this manual.

VI. EXAMPLE CALCULATIONS

1. Estimation of Emission Rates from Surface Impoundments

Wastewater being treated in a secondary biological treatment facility was analyzed for its toxic compounds. The following data were obtained:

Compound	Concentration (mg/L)
Benzene	20
Acrylonitrile	3
Chloroform	10
Perchloroethylene	1

The treatment basin has a surface area of 0.25 acre, about 10% of which is estimated to be the effective zone of turbulence. Estimate the emission rates from the surface impoundment. Assume the data presented in Appendix C can be used wherever applicable for this example.

The gas and liquid phase mass transfer coefficients for convective and turbulent zones can be calculated using Equations (27) - (30). Specific examples for benzene (MW=78.1) at 25°C is given below.

i) Convective zone

a) Liquid phase

$$k_{L,i} = \left(\frac{32}{78.1}\right)^{0.5} \left(\frac{273 + 25}{298}\right) 1.23 \times 10^{-4}$$

$$= 7.87 \times 10^{-5} \quad \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

b) Gas phase

$$k_{g,i} = \left(\frac{18}{78.1}\right)^{0.335} (1)^{1.005} \; 5.8 \times 10^{-5}$$

$$= 3.55 \times 10^{-5} \quad \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

ii) Turbulent (or Aerated) zone

a) Liquid phase

$$k_{L,i} = \left(\frac{32}{78.1}\right)^{0.25} \frac{1.024^{25-20}}{1.024^{5}} (1)^{0.5} \; 0.13$$

$$= 0.1 \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

b) Gas phase

$$k_{g,i} = \left(\frac{18}{78.1}\right)^{0.25} (1)^{0.92} \; 9.5 \times 10^{-4}$$

$$= 6.58 \times 10^{-4} \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

We need to know the value of vapor-liquid equilibrium constant, K, to combine the gas-phase and liquid-phase mass transfer coefficients. From the example given in the appendix, one can get K = 308 for benzene at 25°C. The overall liquid phase mass transfer coefficients in the convective ($(K_L)_C$) and turbulent ($(K_L)_T$) zones are calculated using Equation (4).

$$\frac{1}{(K_L)_C} = \frac{1}{7.87 \times 10^{-5}} + \frac{1}{308 \times 3.35 \times 10^{-5}} = 1.28 \times 10^{4}$$

$$(K_L)_C = 7.81 \times 10^{-5} \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

$$\frac{1}{(K_L)_T} = \frac{1}{0.1} + \frac{1}{308 \times 6.58 \times 10^{-4}} = 14.9$$

$$(K_L)_T = 0.067 \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

Use of Equation (13) yields the area-averaged overall mass transfer coefficients,

$$K_L = 7.81 \times 10^{-5} (0.9) + 0.067 (0.1) = 0.0067 \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

Note: overall liquid pahse mass transfer coefficient given in gr-mol/cm^2·sec can be converted to the unit of cm/sec, or 1/sec as follows (See Appendix F for derivation):

density of the wastewater = 1 gr/cm^3

$$K_L \text{ (in cm/sec)} = \frac{0.0067 \times 18}{1} = 0.12 \text{ cm/sec}$$

or if the depth of the surface impoundment is 365.8 cm(12 ft),

$$K_L \text{ (in 1/sec)} = \frac{0.12}{365.8} = 3.3 \times 10^{-4} \text{ 1/sec}$$

The concentration of benzene in mg/L can be converted to mole fraction:

$$x_i = \frac{20}{10^3} \times \frac{1}{10^3} \times \frac{1/78.1}{1/18}$$

$$= 4.61 \times 10^{-6}$$

Equation (5) is used to calculate the emission rate for benzene

$$Q_i = 78.1\ (0.0067)\ (0.25 \times 4047 \times 10^4)\ (4.61 \times 10^{-6})$$

$$= 24.4 \text{ gr/sec}$$

Similar calculations will yield the emission rate for other toxic components.

2. Estimation of Emissions from the Biological Treatment System When Only the Influent Concentration is Known.

Rework Problem 1 given above assuming that the concentrations are for the components in the waste prior to treating in the biological system.

For the compounds under consideration, the adsorption constant (K_1) is near zero in Appendix E and hence the adsorption on sludge is assumed to be negligible. For a continuous aerator with air stripping and biological degradation, Equation (20) can be used for determining the effluent concentration.

$$Se = \frac{S_o}{1 + \frac{k_{1(s)}\ X}{S_o}(1+r)\ t_c + (1+r)\ k_a\ t_c},$$

The nomenclatures are given in deriving equation (20). For industrial bio-treatment, the values of $r=0.4$ and $W=0.013$ are used.

The overall mass transfer coefficient for benzene in Problem 1 is obtained as

$$K_L = 0.0067 \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}},$$

or

$$k_a = 0.0067\ (18) \times \frac{1}{1} \times \frac{1}{12 \times 30.48} \times 86400$$

$$= 28.5\ \text{1/day}$$

At 8 hour retention time and 20 ppm benzene influent concentration, the effluent concentration is

$$Se = \frac{20{,}000}{1 + \frac{3922}{20{,}000}(1+0.4)\frac{8}{24} + (1.04)(28.5)\frac{8}{24}}$$

$$= 1390\ \text{ug/L, or } 1.39\ \text{mg/L.}$$

$$x_i = \frac{1.39}{10^6} \times \frac{18}{78.1} = 3.2 \times 10^{-7} \text{ mole fraction}$$

$$Q_i = 78.1\ (0.0067)(0.25 \times 4047 \times 10^4)(3.2 \times 10^{-7})$$

$$= 1.7\ \text{gr/sec.}$$

Hence the emission rate of benzene from the aerated lagoon is estimated at 1.7 gr/sec. Similar calculations can be performed to obtain the emission rates for other components.

Percent removal by biodegradation and air stripping is:

$$\frac{20-1.39}{20} \times 100 = 93.1\%$$

Fraction of the removal due to each of the multimedia is

i) Bio-degradation

$$\frac{\frac{3922}{20000}(1.4)\frac{8}{24}(1390)}{\frac{3922}{20{,}000}(1.4)\left(\frac{8}{24}\right)(1390) + (28.5)(1.4)\frac{8}{24}(1390)} \times 100 = 0.68\%$$

ii) Removal by air stripping is 99.32%.

3. Estimation of Emission Rates from Landfills

i) Hazardous waste is to be landfilled. The proposed 1/2 acre landfill will be covered by a soil layer of 30 cm above the hazardous waste section. The laboratory tests on soil show an average yearly porosity of 0.16. The vapor in equilibrium with the waste was analyzed for the compounds among the list of carcinogenic evidence using the head space method. The results of the analysis are:

Compound	Concentration in Vapor Space (% by volume)	Equilibrium PARTIAL PRESSURE mmHg
Benezene	0.96	7.3
Trichloroethylene	0.149	1.13
Ethylene Dichloride	0.916	6.96

Estimate the emission rates from the landfill.

For small air phase resistance ($C_{i0} \cong 0$). Equation (35) can be rewritten as

$$Q_i = 4047 \times 10^4 \quad D_i \, P_T^{4/3} \quad \frac{C_i^*}{h} \cdot \bar{A}$$

where Q is the emission rate, gr/sec, and $\bar{A}$ is the landfill area, acres.

$$D_i = 0.088 \text{ cm}^2/\text{sec}$$

The concentration of benezene in the vapor in equilibrium with the waste is calculated from Equation (41).

$$C_i^* = \frac{7.3}{62363} \; \frac{(78.1)}{(298)} = 3.07 \times 10^{-5} \text{ gr/cm}^3$$

Hence

$$Q_i = 4047 \times 10^4 \; (0.088)\,(0.16)^{4/3} \; \frac{3.07 \times 10^{-5}}{30} \cdot 0.5 = 0.16 \text{ gr/sec}$$

Similar calculations will give the emission rates for trichloroethylene and ethylene dichloride.

Q_i for trichloroethylene = 0.034 gr/sec

Q_i for ethylene dichloride = 0.18 gr/sec

ii) For the proposed landfill in example i above, analyses were performed on the waste, instead of its equilibrium vapor, to determine the composition. The results of the analysis are:

Benzene	3% by weight
Trichloroethylene	1% by weight
Ethylene dichloride	4% by weight
Specific gravity of the waste	0.9 gr/cm^3
Molecular weight of the waste	200

Compute the emission rates of each component.

The emission rates can be estimated using either Equation (46), or Equation (35) along with Equations (41) and (42). The use of Equation (46) will be demonstrated here. The use of Equation (35) will be shown in Example iii that follows.

Equation (46) is rewritten as

$$Q_i = 4047 \times 10^4 \; D_i \; P_t^{\;4/3} \; \bar{A} \; \gamma_i \; C_{si} \; \frac{x_i}{\bar{h}}$$

Now for benzene

$D_i = 0.088 \; cm^2/sec$

$\gamma_i = 1$ (assumed to be 1 for hydrocarbon mixtures. See Appendix A for other types of mixture)

P_i^o; vapor pressure of benzene @ 25° C = 95 mmH_g

From Equation (40), $C_{si} = \dfrac{P_i^o \; MW_i}{R \; T}$

$$= \frac{95\ (78)}{62,363(298)} = 0.0004 \; \frac{gr}{cm^3}$$

$x_i = \dfrac{0.03}{78.1}$ (200) = 0.0768 mole fraction and also $P_T^{4/3} = (0.16)^{4/3} = 0.0869$

$\overline{A} = 0.5$ acre

Hence $Q_i = 4047 \times 10^4 (0.088)(0.869)(0.5)(1)(0.0004)\left(\frac{0.0768}{30}\right)$

The emission rates for trichloroethylene and ethylene dichloride can be estimated similarly.

(iii) The proposed landfill in example i above is redesigned to employ a soil cover with thickness of 60 cm. Polyethylene film (thickness 0.03 cm) will be placed between the waste and the cover. Analyses performed on the waste for Example ii will be used for this example. The soil tests showed an annual average moisture content of 19% at a bulk density of 1.15 gr/cm^3. Evaluate the landfill as before.

The polyethylene film can be converted to equilibrium soil thickness. The use of Equation (22) to obtain the thickness of soil corresponding to bulk density of 1.19 gr/cm^3 and a soil mixture content of 20% gives

$$h_{eq} = 134.6\ h_f$$

$$= 134.6\ (0.03) = 4 \text{ cm}$$

The air-filled porosity and total porosity of the soil are

$$P_a = 1 - \frac{1.15}{2.65} - 0.19\ (1.15) = 0.348$$

$$P_T = 1 - \frac{1.15}{2.65} = 0.566$$

$$P_a^{10/3} / P_T^2 = 0.348^{10/3}/0.566^2 = 0.0925$$

The partial pressure p_i^* of each component i in equilibrium with the waste can be estimated by Equation (42):

$$p_i^* = \gamma_i\ \overset{o}{P}_i\ x_i$$

where γ_i is the activity coefficient of component i (assumed to be 1 in hydrocarbon mixtures), P_i^o is the vapor pressure of component i, mmHg, P is the total pressure, 760 mmHg, x_i is the mole fraction of component i in the waste.

1) benzene (3 % by weight)

x_i = 0.0768 mole fraction

p_i^* = 0.0768 (95) = 7.3 mmHg

Similarly

2) trichloroethylene

p_i^* = 1.13 mmHg

3) ethylene dichloride

p_i^* = 7 mmHg

Hence the equilibrium vapor phase concentrations can be computed using Equation (41).

C_i^* for benzene = 3.07×10^{-5} gr/cm^3

Note that $C_i^* = C_{si} \cdot x_i$ in this case (for hydrocarbon mixture due to the assumption of $\gamma_i \cong 1$)

C_i^* for trichloroethylene = 8×10^{-6} gr/cm^3

C_i^* for ethylene dichloride = 3.73×10^{-5} gr/cm^3

Use of Equation (53) yields the estimated emission rate

$$Q_i \text{ for benzene} = 0.088 \left[\frac{1}{\frac{60}{0.0925} + 1962.8(0.03)} \right] (3.07\text{x}10^{-5})\,0.5\,(4047\text{x}10^{4})$$

$$= 0.077 \text{ gr/sec}$$

Q_i for trichloroethylene = 0.016 gr/sec

Q_i for ethylene dichloride = 0.084 gr/sec

iv) The wastes in Examples ii and iii are to be landfilled after mixing with municipal garbage. Estimate the emission rates for each case.

a) Example ii with gas generation

The gas generated as result of decomposition of the garbage will contribute to additional release of hazardous air pollutants. The emission rate will be estimated from Equation (47) at an average velocity of generated gas 1.63×10^{-3} cm/sec in the landfill (17). To use Equation (47) the concentration at the interface, C_{io}, must be known. An expression for it can be obtained by equating Equation (47) and Equation (48), or

$$C_{io} = \frac{C_i^* \exp\left(\frac{h \cdot \bar{V} \cdot \tau}{D_i \cdot \epsilon}\right)}{1 + \frac{k_{g,i}\,(2.44\text{x}10^4)}{\bar{V}} \left(\exp\left(\frac{h \cdot \bar{V} \cdot \tau}{D_i \cdot \epsilon}\right) - 1\right)} \qquad (67)$$

The gas-phase mass transfer coefficients required in Equation (67) are obtained from the relationship given by Equation (28),

$$k_{g,i} \text{ for benzene} = \left(\frac{MW_{H_2O}}{MW_i}\right)^{0.335} \left(\frac{273 + 25}{298}\right)^{1.005} k_{g,H_2O}$$

$$= \left(\frac{18}{78.1}\right)^{0.335} 5.8 \times 10^{-5} = 3.55\text{x}10^{-5} \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

Similarly,

$k_{g,i}$ for trichloroethylene = 3.0×10^{-5} gr-mol/cm$^{2}\cdot$sec

$k_{g,i}$ for ethylene dichloride = 3.29×10^{-5} gr-mol/cm$^{2}\cdot$sec

The interface concentrations are

1) Benzene

$$\frac{h \cdot \bar{V} \cdot \tau}{D_i \cdot \epsilon} = \frac{30(1.63\times10^{-3})(1.73)}{0.088(0.16)} = 6.01$$

$$C_{io} = \frac{3.07\times10^{-5} \quad e^{6.01}}{\dfrac{1 + 3.55 \times 10^{-5}\ (2.44\times10^{4})}{1.63\times10^{-3}} (e^{6.01} - 1)}$$

$$= 5.79\times10^{-8} \text{ gr/cm}^3$$

2) trichloroethylene

$D_i = 1.5\times10^{-4}\ (1/131.4)^{0.5}\ 298^{1.5} = 0.067$

$C_{io} = 1.78\times10^{-8}$ gr/cm^3

3) ethylene dichloride

$D_i = 0.078$

$C_{io} = 7.58\times10^{-8}$ gr/cm^3

Hence the emission rates estimated from Equation (47) are

1) Benzene

$$Q_i = \left[1.63\times10^{-3}\ \frac{3.07\times10^{-5} - 5.79\times10^{-8}}{e^{6.01} - 1} + 1.63\times10^{-3}\ (3.07\times10^{-5}) \right] (0.5)$$

$$\times\ (4047\times10^{4}) = 1.02 \text{ gr/sec}$$

2) Trichloroethylene

$Q_i = 0.26$ gr/sec

3) Ethylene dichloride

$Q_i = 1.22$ gr/sec

b) Example iii with gas generation

Equation (54) will be used to estimate the emission rates. As seen above, $C_{io} << C^*_i$. Hence C_{io} can be neglected in Equation (54). The emission rate for benzene is

$$Q_i = \left[1.63x10^{-3} \frac{3.07 \times 10^{-5}}{\exp\left[\frac{1.63x10^{-3}}{0.088}\left(\frac{60}{0.0925} + 1962.8(0.03)\right)\right] - 1} + 1.63x10^{-3}\ (3.07x10^{-5}) \right] (0.5)(4047x10^4) = 1.01 \text{ gr/sec}$$

Similarly

Q_i for trichloroethylene = 0.26 gr/sec

Q_i for ethylene dichloride = 1.22 gr/sec

V. Estimation of Emission Rates from Land Treatment Facilities

An oily waste is treated in a one acre landfarm by subsurface injection at an application rate of 1.5 $\#/ft^2$. The depth of injection is 5" (12.7 cm). The waste analysis shows the presence of benzene in the oil at a level of 1500 ppm by weight. The porosity of the soil in the cultivation layer is determined to be 0.35 by test. Estimate the average emission rates. Other pertinent information:

Average MW of the waste: 200

Sp. gr. of the waste: 0.9 gr/cm^3

Cultivation layer soil bulk density: 0.8 gr/cm^3

The use of Equation (55) requires the concentration of benzene on the vapor side of the oil-vapor interface, which can be calculated from Equation (56).

The initial concentration of benzene in the oil

$$C_{iwo} = \frac{1500}{10^6/0.9} = 1.35x10^{-3}\ gr/cm^3$$

When the wind is blowing toward the downwind monitor, the concentration at the downwind monitor is estimated to be

$$3570 + 0.1 \cong 3570 \ \frac{\mu gr}{m^3}$$

The impact of the facility on the downwind population located at say 500 m from the facility can be predicted similarly. If the frequency of wind blowing toward the population is 0.25, the net concentration is

$$\chi = \frac{16}{2\pi\,(580)} \, \frac{2(20.9)}{\sqrt{2\pi}\,(18.6)(5)} \, (0.25) = 1.97 \times 10^{-4} \ \frac{gr}{m^3}$$

$$\left(= 197 \ \frac{\mu gr}{m^3} = 179 \text{ ppb}\right)$$

To evaluate whether or not this concentration is within the acceptable level recommended in the other criteria goals, the drinking water standard obtained from analysis of toxic effects data, which is protective of human health against the ingestion of contaminated water, is used. This standard is 200 μg/L. Based on daily consumption of 2 L of water and 20 m^3 of air, the acceptable ambient air concentration of cyanide is calculated as

$$\frac{200 \ \frac{\mu gr}{L} \ 2 \text{ L}}{20 \ m^3 \times 0.6} = 33.3 \ \frac{\mu gr}{m^3} \ (\ = 30.1 \text{ ppb by volume})$$

where it is assumed that only 60% of the inhaled cyanide is absorbed. The average concentration impacting the population is higher than the acceptable value.

NOMENCLATURE

A : surface area of disposal facility, cm^2

a_s : interfacial area per unit volume of soil for the oily waste, cm^2/cm^3

a_V : surface area per unit volume of surface impoundment, ft^{-1}

C_{ig}, C_{iL}: concentration of gas and liquid phases at the gas liquid interface in the pore, gr/cm^3

C_{iWD}: initital concentration of component i at the soil-air interface, gr/cm^3

C_{io} : concentration of component i in the air far away from the soil-air interface, gm/cm^3

$C_{i\infty}$: concentration of component i in the air far away from the soil-air interface, gr/cm^3

C_i^* : concentration of component i in the air space at the immediate vicinity of the waste (or in equilibrium with the waste), gr/cm^3

C_m : maximum permissible concentration, $\mu gr/m^3$

D : diffusion coefficient, cm^2/sec (note: D_{i,H_2O} means the diffusion coefficient of component i in water)

D_{ei}: effective diffusivity of component i in the air-filled soil pore, cm^2/sec

D_{wi}: diffusivity of component i in the waste, cm^2/sec

d : diameter of aerator turbine or impeller, ft

d_e : effective diameter of quiscent area of surface impoundment, m

d_p : soil clump diameter, cm

g : gravitational or conversion constant, ft/sec^2

H : Henry's law constant, $atm/mol/m^3$

H_c : Henry's law constant in concentration ($C_{ig} = H_c C_{iL}$)

H_o : effective depth of surface impoundment, ft

h : depth of soil cover, cm

h_{eq}: soil equivalent to polyethylene film

h_f : polyethylene film thickness, cm

h_p : depth of penetration by soil contamination below the surface, cm

h_s : depth of subsurface injection, cm

J : oxygen transfer rating of surface aerator, normally about 3 lb O_2/hr-hp

K : vapor-liquid equilibrium constant

K_1, K_T: adsorption constants

K_L : overall mass transfer coefficient, gr-mol/$cm^2 \cdot sec$

k_g, k_L: gas and liquid phase mass transfer coefficients, resp., gr-mol/$cm^2 \cdot sec$

$k_{g,i}$: gas phase mass transfer coefficient of component i in air, gr-mol/$cm^2 \cdot sec$

$k_{L,i}$: liquid phase mass transfer coefficient of component i in a surface impoundment, gr-mol/$cm^2 \cdot sec$

$k_{1(s)}$: biodegradation rate constant in Grau model ($n=1$), 1/day.

L : distance from center of a disposal facility to property line, m

L_v : virtual downwind distance to receptor ($L' + L$), m

L' : distance from virtual point to center of a disposal facility, m

M_T : amount of waste application, gr

m_{io}: initial amount of component i placed for landfarming, gr

MW : molecular weight

N_{FR}: Froude number, $d\,\omega^2/g$

N_p : power number, $P_r\ g/\ \rho_L\ d^5\ \omega^3$

N_{Re}: gas Reynolds number, $\rho_g\ d^2 \omega / \mu_g$

N_{SC}: gas Schmidt number, $\mu_g/\ \rho_g\ D_{i,air}$

p : partial pressure, mmHg

P : total pressure, mmHg

P^o : pure component vapor pressure, mmHg

P_a : air-filled porosity, cm^3/cm^3

P_T : total porosity, cm^3/cm^3

POWR: total power input to aerators in the aerated surface impoundment, Hp

P_r : power to impeller, ft-lb force/sec

Q : rate of emissions from a disposal facility, gr/sec, or flow rate to biological treatment where defined, L/day

q : emission rate per unit area of the area source, $gr/cm^2 \cdot sec$

R : gas constant, $cm^3 \cdot mmHg/^oK \cdot mol$

Re^* : roughness Reynolds number (See Reference 4 for the expression)

Ru : unit risk

r : recycle ratio

S : width of area source, m, or substrate concentration where defined ug/L.

T : temperature, ^oK

t : time, sec

t_c : hydraulic residence time, day

t_d : dry-out time, sec

U_o : surface velocity, ft/sec, normally 0.035 x wind speed (ft/sec) for natural surface, ft/sec, and 0.1 ft/sec for outside of region of effect of aerators in the biological treatment

u : wind speed, m/sec

U_{air}: wind speed:, m/hr

V : volume of surface impoundment in region of effect of aerators, ft^3

$\overline{V}$: average gas velocity in the soil pore in the upwind direction, cm/sec

w : soil water content, gr/gr

w_f : fraction of oil in film form on soil

X : sludge concentration, ug/L

X' : maximum amount of the substrate adsorbed on sludge, ug/L.

x : liquid phase mole fraction

y : gas phase mole fraction

z_o : oil layer diffusion length, cm

Greek Letter

α : oxygen transfer correction factor

μ : viscosity, gr/cm·sec

χ : net ambient concentration of a hazardous substance originated from disposal facility emissions, gr/m^3

σ_z: standard deviation of the concentration distribution in the vertical direction, m

ϕ : relative frequency of occurence from stability wind rose

θ : temperature, ^{o}C

γ : activity coefficient

ρ : density, lb/ft^3

$\bar{\rho}$: density, gr/cm^3

ω : rotational speed of turbine impeller, rad./sec

Subscript

air : air

c : convective

H_2O: water

g : gas

i : hazardous component i

j : hazardous component j

L : liquid

O_2 : oxygen

p : soil particle

T : turbulent

Tol: toluene

w : waste

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PART A
APPENDICES

Appendix A

Methods for Determining K-values

1. From Experimental Data:

The liquid sample taken from a surface impoundment can be equilibrated in a head space, and the liquid and vapor phases can be analyzed for concentrations of each hazardous component. The K-value is

$$K = y_i/x_i \qquad \text{(A-1)}$$

where K is the K-value or the vapor-liquid equilibrium constant, y_i is the mole fraction of hazardous component i in the vapor phase, and x_i is the mole fraction of hazardous component i in the liquid phase. When the partial pressure (p_i, mmHg) of component i in the vapor phase is measured, $y_i = p_i/P$ where P is the total pressure, mmHg.

The K-values determined this way are valid at the applicalbe liquid concentrations and temperature. If Henry's or Raoult's laws hold for the liquid mixtures, the K-value could be used over a range of concentrations.

2. From Henry's Law Constant:

Henry's law often holds for aqueous solutions of sparingly soluble organic compounds. Examples are benzene, chloroform, etc. in wastewater. Henry's law constants are expressed in several different units. A collection of Henry's law constants in atm/(mol/m^3) is attached here with (Table A-1). Other Henry's law constants may be found in a handbook. The K-value can be determined by one of the following ways:

$$K = \frac{H\left(\frac{\text{atm}}{\text{mol/m}^3}\right) \times 10^6}{P(\text{atm})\ MW_{av}} \qquad \text{(A-2)}$$

Table A-1 SUMMATION OF DATA FOR HENRY'S LAW CONSTANT

Compound	Vapor Pressure atm.x 10^{-3}	Temp. ^{o}K	Solubility g/m^3	Temp. ^{o}K	Molecular Weight g/mol	H, m^3 atm/mol x 10^{-3} Calculated	H, m^3 atm/mol x 10^{-3} Experimental
Acenaphthene	- -	-	3.93	298	154.2	- -	0.241
Benzene	125	298	1780	298	78.1	5.48	5.55
Carbon tetrachloride	149	298	800	298	153.8	28.6	30.2
Chlorobenzene	15.5	298	472	298	112.6	3.70	3.93
1,2,4-Trichlorobenzene	0.383	298	30	-	181.5	2.32	1.42
Hexachlorobenzene	- -	-	0.006	298	284.8	- -	1.70
1,2-Dichloroethane	113*	298	8300	298	99.0	1.35	1.10
1,1,1-Trichloroethane	168*	298	6497*	298	133.4	4.08	4.92
Hexachloroethane	- -	-	50	295	236.7	- -	9.85
1,1-Dichloroethane	308	298	5500	293	99.0	5.54	5.45
Chloroform	260	298	9600	298	119.2	3.23	3.39
1,2-Dichlorobenzene	1.97	298	145	298	147.0	2.00	1.94
1,3-Dichlorobenzene	2.48	298	123	298	147.0	2.96	2.63
1,4-Dichlorobenzene	- -	-	79	298	147.0	- -	2.72
1,1-Dichloroethylene	778	298	5000	293	97.0	15.1	15.0
1,2-trans-Dichloroethylene	263	287	6300	293	96.9	4.05	5.32
1,2-Dichloropropane	65.8	298	2700	293	113.0	2.75	2.82
1,3-Dichloropropylene	32.9	293	2700	298	111.0	1.35	3.55
Ethylbenzene	12.5	298	206	298	106.2	6.44	6.44
Methylene chloride	599*	298	16700	298	84.9	3.04	3.19
Bromoform	7.37	298	3130*	298	252.8	0.595	0.532

(cont'd) SUMMATION OF DATA FOR HENRY'S LAW CONSTANT

Compound	Vapor Pressure atm. x 10^{-3}	Temp. ^oK	Solubility g/m^3	Temp. ^oK	Molecular Weight g/mol	H, m^3 atm/mol x 10^{-3} Calculated	H, m^3 atm/mol x 10^{-3} Experimental
Bromodichloromethane	- -	-	- -	-	163.8	- -	2.12
Trichlorofluoromethane	833*	298	1100	298	137.4	104	58.3
Dibromochloromethane	65.8	293	- -	-	168.8	- -	0.783
Hexachlorobutadiene	0.197	293	2	293	260.8	25.7	10.3
Hexachlorocyclopentadiene	0.107	298	0.805	298	272.7	36.2	16.4
Nitrobenzene	0.374	298	2000	298	123.1	0.023	0.024
4,6-Dinitro-o-cresol	- -	-	- -	-	198.1	- -	0.0014
Phenol	- -	-	67000	298	94.1	- -	0.0013
Acenaphthylene	- -	-	3.93	298	152.2	- -	0.114
Fluorene	- -	-	1.98	298	116.2	- -	0.117
Tetrachloroethylene	25.8*	298	150	298	165.8	28.5	28.7
Toluene	37.4	298	535	298	92.1	6.44	5.93
Trichloroethylene	97.8	298	1100	298	131.5	11.7	11.7
Aldrin	- -	-	0.2	293	364.9	- -	0.496
Dieldrin	- -	-	0.186	298	380.9	- -	0.058
Chlordane	- -	-	1.85	298	409.8	- -	0.048
Heptachlor	- -	-	0.056	298	373.4	- -	1.48
Heptachlor epoxide	- -	-	0.275	298	389.3	- -	0.032
Arochlor 1254	- -	-	0.012	298	328.4	- -	8.37
Toxaphene	- -	-	1.75	298	413.9	- -	4.89

* Data interpolated between two data points. - Data unavailable.

or

$$K = \frac{H\left(\frac{\text{atm}}{\text{mol/m}^3}\right)}{R\left(\frac{\text{m}^3\ \text{atm}}{\text{mol}\ ^\circ\text{K}}\right)T(^\circ\text{K})}\ \frac{C_{liquid}\left(\frac{\text{lb-mol}}{\text{ft}^3}\right)}{C_{gas}\left(\frac{\text{lb-mol}}{\text{ft}^3}\right)} \qquad \text{(A-3)}$$

where P is the total pressure, atm, $MW_{av.}$ is the average molecular weight of solution, R is the gas constant ($8.2\times10^{-5}\ \frac{\text{m}^3\ \text{atm}}{\text{mol}\ ^\circ\text{K}}$), T is the temperature, °K, C_{liquid} is the liquid density , lb-mol /ft^3, and C_{gas} is the gas density, lb-mol/ft^3.

Example

Henry's law constant for benzene in water is 5.55×10^{-3} atm/(mol/m^3) at 25°C. Calculate the K-value by Equations (A-2) and (A-3).

1. Equation (A-2)

$$K = \frac{5.55 \times 10^{-3} \times 10^{6}}{(1)(18)} = 308.3$$

2. Equation (A-3)

$$C_{liquid} = 62.4/18 = 3.467 \text{ lb-mol/ft}^3$$

$$C_{gas} = \frac{P}{RT} = \frac{14.7}{10.73(460+77)} = 0.00255 \text{ lb-mol/ft}^3$$

$$K = \frac{5.55 \times 10^{-3}}{8.2 \times 10^{-5}(298)}\ \frac{3.467}{0.00255} = 308.5$$

3. From Raoult's Law

Raoult's law often holds for hydrocarbon mixtures. The K-value can be calculated by

$$K = \frac{P_i}{P} \qquad \text{(A-4)}$$

where P_i is the vapor pressure of a hazardous component at a temperature of concern, mmHg, and P is the total pressure.

3. Other cases:

When Henry's law constants are not available or the Raoult's law does not hold for the mixture, the K-value can be obtained by

$$K_i = \frac{\gamma_i P_i}{P} \qquad \text{(A-5)}$$

where γ_i is the activity coefficient, P_i is the vapor pressure of a hazardous component, mmHg, P is the total pressure, mmHg. There are methods of determining the activity coefficients for aqueous solutions and hydrocarbon mixtures. These methods are not discussed here. If γ is close to unity as in the case of hydrocarbon mixtures, Equation (A-5) becomes Raoult's law. If γ is not close unity but remains constant at low concentrations, Equation (A-5) becomes Henry's law.

4. Henry's law constant in concentration:

The Henry's law constant (H_c) expressed in concentration unit occurs in problems involving landfarming. The constant is related by

$$C_{ig} = H_c \cdot C_{iL} \qquad \text{(A-6)}$$

where C_{ig}(gr/cm3) and C_{iL} (gr/cm3) are concentrations on the gas and liquid side of the oil-air interface in the soil pore spaces. H_c is related to H or K as follows:

$$H_c = H\left(\frac{\text{atm}}{\text{gr-mol/m}^3}\right) C_g\left(\frac{\text{gr-mol}}{\text{cm}^3}\right) \frac{10^6}{P(\text{atm})} \qquad \text{(A-7)}$$

and

$$H_c = K \cdot C_g \left(\frac{\text{gr-mol}}{\text{cm}^3}\right) \frac{MW_{av.}}{\bar{\rho}_w}$$

where C_g is the molar density of vapor ($1/2.44 \times 10^4$ gr-mol/cm^3), $MW_{av.}$ is the average molecular weight of oil, and $\bar{\rho}_w$ is the density of the oil, gr/cm3.

APPENDIX B

DRAFT

A MODEL FOR VOLATILE CHEMICAL EMISSIONS TO AIR FROM LANDFARMING OF OILY WASTES

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An overview of petroleum industry landfarming operations for disposal and treatment of organic waste was given by Knowlton and Rucker (1). The land is cultivated to provide a continuing supply of oxygen. Water and fertilizer are added, if needed. The end products of landfarming are carbon dioxide, water, and increased humus content of the soil. The most common wastes treated within the petroleum industry are oily sludges and biosolids.

Typically a heavy oily sludge is spread several inches thick. The soil is then cultivated at frequent intervals for about two months. Vacuum trucks apply free flowing oil waste directly to the land. Heavy, solidified wastes are distributed over the landfarm from dump trucks and spread with a bulldozer. Cultivation of the waste into the soil is done with various kinds of farm implements.

Application rates vary widely from 200 to more than 600 barrels per acre per year. The application thickness can vary from several inches to a thin layer of a fraction of an inch. Avoiding clumps and spreading as a uniform layer as possible makes subsequent cultivation most effective. The cultivation depth is usually the top six inches of soil. Refinery waste suitable for landfarming are: tank cleanings with 20 to 50 percent oil, separator cleanings with 10 to 20 percent oil, other cleanings with approximately 10 percent oil, a wastewater treatment plant sludge zero % and filter clays with approximately 8 percent oil.

To evaluate the extent of atmospheric emission of volatile chemicals from landfarming oprations transport mechanisms from the soil surface and the soil pore spaces must be considered. During the time the oily waste is placed upon the soil and cultivated, vaporization can occur directly from the surface. The exposed liquid or semi-solid contains volatile component i of mole fraction x_i. The vapor concentration, C_i^* of this chemical in equilibrium with the oily waste is:

$$C_i^* = \frac{\gamma_i \, P_i^o \, MW_i}{R\,T} \qquad (1)$$

where MW_i is molecular weight of the volatile chemical, P_i^o is pure component vapor pressure, γ_i is the liquid phase activity coefficient, R is the gas constant and T is absolute temperature. The flux rate from the surface is:

$$q_i = k_{g,i} \, C_i^* \, MW_i \qquad (2)$$

where q_i is in $gr/cm^2 \cdot s$, $k_{g,i}$ is the gas phase mass transfer coefficient in $gr\text{-}mol/cm^2 \cdot sec$ and C_i^* is in gr/cm^3. The rate equation assumes no mass transfer resistance in the oil phase. This assumption will be valid only for a very short period of time, as the volatile chemical species is lost from the surface molecules need to be replaced from the lower liquid layers and hence the resistance increases. Eq. (2) however, provides an estimate of the maximum volatilization rate. See Thibodeaux (2) for the development of a model for the evaporation of liquid chemicals spilled or otherwise placed on land.

Soil Pore-space Evaporation and Diffusion Model

A model for the vaporization and movement of pure liquid spilled on a dry soil has been presented by Thibodeaux (3). The pure liquid is assumed to soak into the dry soil and contaminates it to a depth h_p. The liquid coats the pore walls and particle junction sites. The chemical evaporates from the interstitial soil surfaces, and the vapor diffuses through the pores upward toward the air-soil interface. In a very short time a hypothetical "dry" zone develps near the surface, and liquid vaporization occurs from the plane formed between this zone and the remaining "wet" zone. As vaporization occurs the dry zone increases in depth and the wet zone decreases. It is further assumed that the soil column is isothermal, that no vertical liquid movement occurs by capillary action, no adsorption on soil particles, and no biochemical oxidation. Equations are developed for the evaporation life time and flux rate. This paper extends the model to the evaporization of chemical species from oil waste mixture in landfarm-type treatment type operations.

Oily wastes are placed on the soil surface or injected below the surface. When placed on the surface the waste is then cultivated into the soil column to the depth of the plow slice h_p(cm). Subsurface injection is done to a depth below the surface h_s (cm), where $h_s \leq h_p$. Figure 1 shows these depths and the relative locations of the "wet" and "dry" zones for volatile species i in the oily waste. The following is a general model which applies to either the surface application or subsurface injection method.

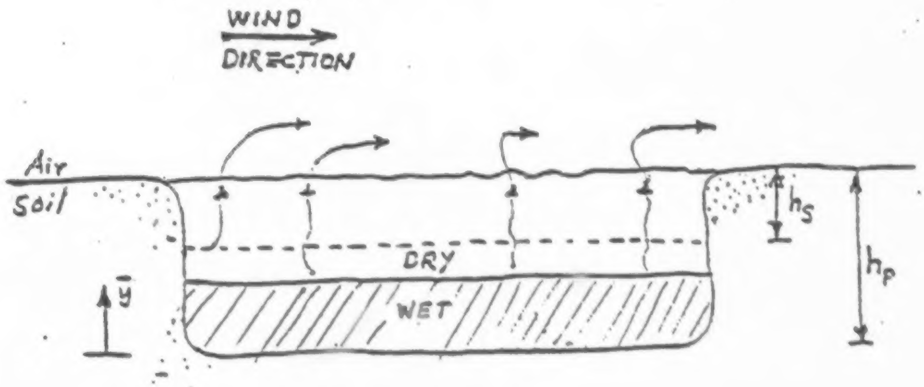


Figure 1 Evaporation and Diffusion from landfarm Soil

Species i in the oily waste mixture exerts a concentration C_{ig} (g/cm^3) while in the wet zone the evaporation diffusion life time t_d for initial mass of i m_{io} (g) incorporated into the zone $h_p - h_s$ is

$$t_d = (h_p + h_s)\, m_{io}/(2\, D_{ei}\, A\, C_{ig}) \tag{3}$$

where D_{ei} (cm^2/s) is the effective diffusivity of i in the air-filled soil pore species and A(cm^2) is the surface area over which oily waste is applied (i.e., m_{io}/A is the application rate). The flux rate, q_i ($g/cm^2 \cdot s$) through the wet-dry interface is

$$q_i = D_{ei}\, C_{ig}/\left[h_s^2 + 2\, D_{ei}\, t\, A\, (h_p - h_s)\, C_{ig}/m_{io}\right]^{1/2} \tag{4}$$

where t is the time after application. For the surface application case $h_s = 0$ in equations 3 and 4. In both cases $t \leq t_d$.

The effective wet zone pore space concentration of species, i, C_{ig} must reflect the diffusion resistance within the oil phase and within the airfilled pore spaces. The rate i moves through the oil phase in the wet zone is equal to the rate i moves from the top of the wet zone to the surface. This equality is:

$$a_s\, A\, \bar{y}(D_{wi}/z_o)(C_{iwo} - C_{iL}) = (D_{ei}\, A/(h_p - \bar{y}))(C_{ig} - 0) \tag{5}$$

where a_s (cm^2/cm^3) is the interfacial area per unit volume of soil for the oily waste, D_{wi} (cm^2/s) is the effective diffusivity of i in the oil. z_o(cm) is the oil layer diffusion length, and C_{iwo} (gr/cm^3) is the initial concentration of i in the oil. For equilibrium at the interface

$$C_{ig} = H_c\, C_{iL} \tag{6}$$

where C_{ig} (g/cm^3) and C_{iL} (g/cm^3) are concentrations on either side of the interface, and H_c (cm^3 oil/cm^3 air) is the Henrys law constant in concentration form. Combining Equations 5 and 6 yields;

$$C_{ig} = \left[\frac{H_c}{1 + H_c\left(\dfrac{D_{ei}\, z_o}{D_{wi}\, a_s\, f(\bar{y})}\right)}\right] C_{iwo} \tag{7}$$

where $f(\bar{y}) = \bar{y}\,(h_p - \bar{y})$ accounts for the lenthening dry zone. The average value of this function during the evaporation diffusion process is

$$f(\bar{y}) = (h_p^2 + h_p\,h_s - 2\,h_s^2)/6 \qquad (8)$$

and should be used to estimate $f(y)$ in Equation (7). For small values of the oil layer coating the soil particles, z_o, or large interfacial area, a_s, Equation 7 reduces to $C_{ig} = H_c\,C_{iL}$ and the process is air pore space diffusion controlled.

Oil mass distribution within the soil column will be assumed to be bidispersed. One fraction of the mass, $f\,m_{io}$, is in "film" form. This fraction, a thin film that coats the soil clumps, is in direct contact with the air filled pore spaces and is readily available for transport to t[illegible]face. The remaining mass is in "lump" form and is $(1-f)m_{io}$. The lump fraction is contained in the dead-end air-filled pore spaces or in the spaces between soil particles. The lumps are relatively large and have low interfacial area so that molecules of i have a more tortu path to the air-filled pore spaces that connect with the surface. Figure 2 shows the bidispersed nature of oil in a soil column. Since approximately half of the pore spaces in soil are air filled (4), f=0.5 seems reasonable as a first approximation.

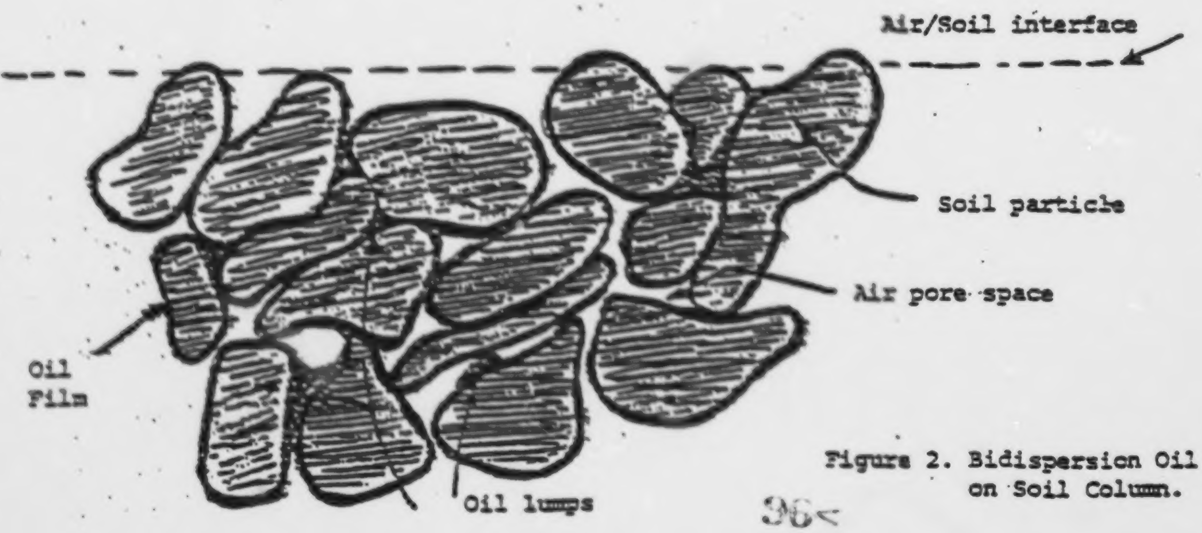
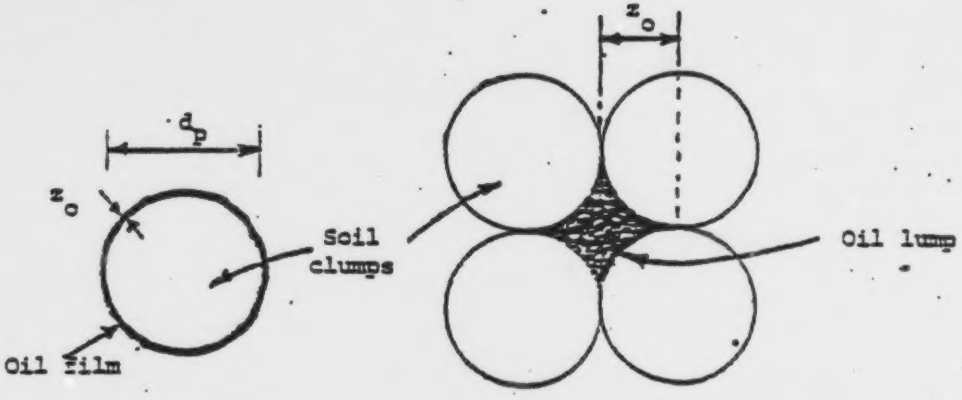


Figure 2. Bidispersion Oil on Soil Column.

Soil with a high degree of organic matter is usually found to have a structure classed as spheroidal clumps (4). These clumps are reported to have diameters up to one half inch. By using spheres and associations of spheres it is possible to construct simple geometric models and estimate the oil phase diffusion path, z_o(cm), and the interfacial area per volume, a_s (cm^2/cm^3), for the film and lump oil forms.



a) film form b) lump form

Figure 3. Sphere Models for Oil Forms in Soil.

Figure 3 shows simple sphere models for oil forms in the soil column.

For oil in film form the thickness or diffusion path length, z_o (cm), is

$$z_o = d_p \ \bar{\rho}_p w_f / 6 \ \bar{\rho}_w \qquad (9)$$

where d_p(cm) is soil clump diameter, $\bar{\rho}_p$ (g/cm^3) is soil clump density, w_f is the fraction of oil in film form on the soil, and $\bar{\rho}_w$ (g/cm^3) is the oil density. The interfacial area for the film form is;

$$a_s = 6/d_p \qquad (10)$$

For oil in lump form the mass will be assumed to be trapped in the space formed by eight spheres in an orthogonal arrangement. Figure 3 shows a two-dimensional view of the lump form model. For diffusion path length for the lump is:

$$z_o = d_p/2 \qquad (11)$$

and the a_s for the lump is:

$$a_s = 2.70/d_p \qquad (12)$$

In the case of bidispersed oil the model equations developed for evaporation and diffusion (i.e., Equations 3,4,7 and 8) apply for each form. Because of relative diffusion path lengths and interfacial areas the dry zone for the film mass fraction will grow faster than that for the lump mass fraction. In other words the life-time for dry-out will be shorter for the film form. The volatile component i in the film form will contribute to initial high flux rates of relative short duration. This is because z_o is small and a_s is large. Volatile component i in lump form will have lower flux rates and larger life-time. This is due to large z_o and lower a_s values. The net result is high initial flux rates contributed to by both oil forms. The average flux rate during time period t is twice the point rate value obtained by Equation 4. The point rate falls as the square root of time. The film form does not contribute to the flux when $t > t_f$. The flux continues to fall until $t = t_L$ (i.e., lumps life-time). The air filled pore spaces still contain vapor of i and this remaining small quantity moves to the surface by vapor diffusion. Thibodeaux (3) presents a model rate edquation that is exponential in form for this period. The time for depleting the soil air filled pore spaces of 90% of the remaining vapor is

$$t_{0.1} = 0.794\, h_p^2 / D_{ei} \qquad (13)$$

The model is capable of handling the emission of multiple volatile components from the oil. This can be done by treating each component individually using the model equations and assuming no interaction or interference between species. The total flux rate is the sum of the individual species flux rates. The total flux for surface application should decrease as $\sqrt{t}$ just as for individual species.

The re-cultivation of the waste treatment area sometime after the first application may result in a temporary increase in the vapor emission rate. If the area is plowed after a period of time t (s) and this period is less than the life-time of species in either film or lump form, the remaining masses in the wet zones are uniformly redistributed in the plow slice. The mass of i, $m_{i\bar{t}}$ (g), volatilized during the period $\bar{t}$ is;

$$m_{i\bar{t}} = 2\, A\, \bar{t}\, q_{i\bar{t}} \qquad (14)$$

where $q_{i\bar{t}}$ (g/cm^2.S) the flux rate of species i at $t=\bar{t}$. The remaining mass, $m_{io} - m_{i\bar{t}}$, is now used in the model equations to compute the flux rates after plowing. The remaining mass contains the initial film and lump from distribution.

Preliminary results from laboratory simulation experiments of landfarming volatile emissions(5) suggests that the model is qualitatively reasonable. Equation 4 shows that concentration in the air above an area, treated by surface application then cultivated, should fall with the $\sqrt{t}$. Emission data where concentration in the air from a laboratory simulation is measured with time should have

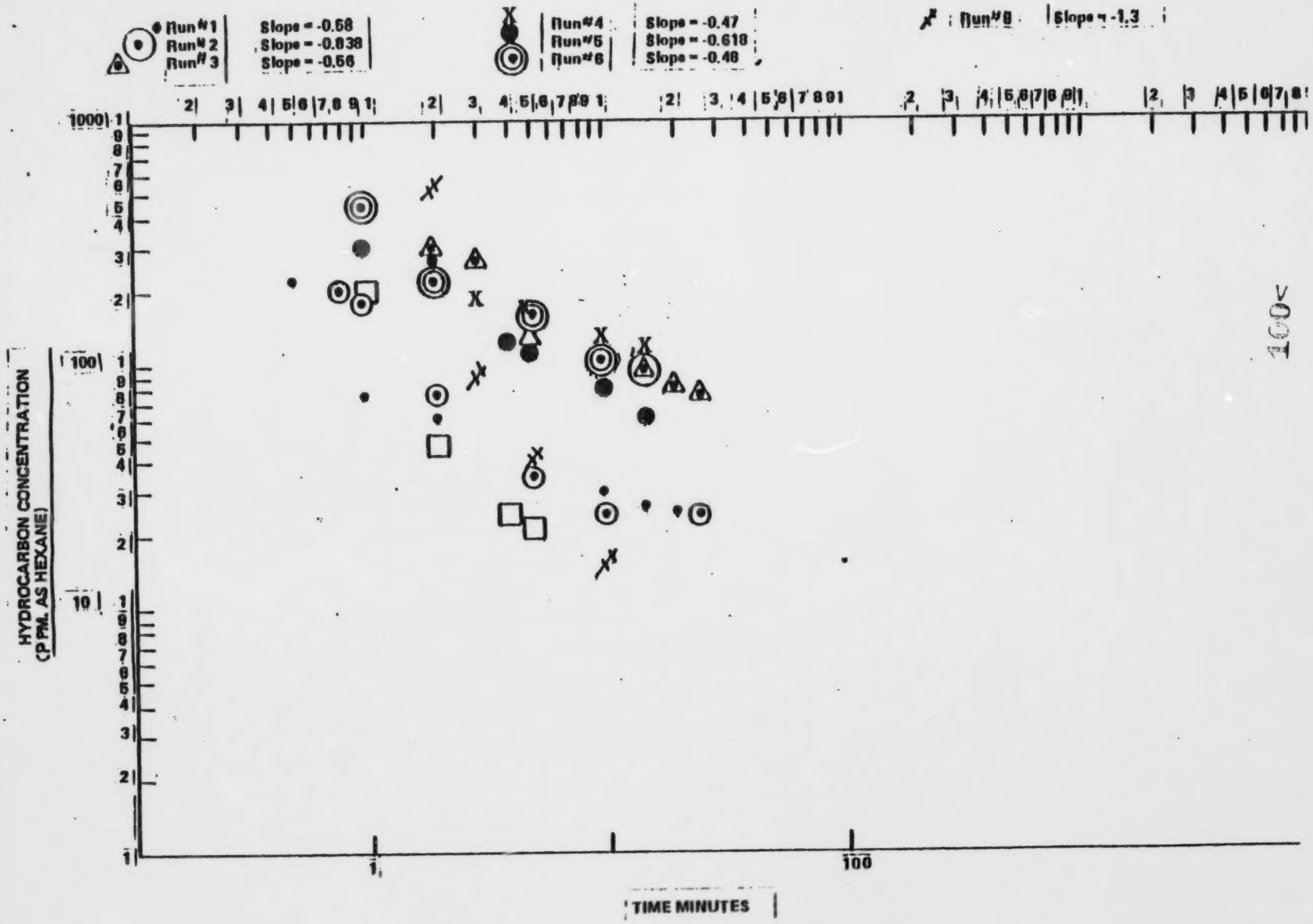


FIGURE 4. CONC. vs TIME

a slope of -0.5. Figure 4 shows the analyzis of some preliminary data for eight experiments. The average slope is -0.68 with a range of -0.39 to -1.3.

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APPENDIX C

Summary of Data Used in Obtaining Mass Transfer Co-efficients in Table 1

1) Natural Surface

  a) Liquid phase

    Av. temp. = 25°C

    Surface velocity = 0.1 ft/s

    Effective depth in the region of aerators = 11.5 ft

  b) Gas phase

    Wind speed = 10 MPH

    Av. temp. = 25°C

    Area of Impoundment = 1/4 acre (10,890 ft^2)

    Effective aeration area = about 10%

2) Turbulent Surface

  a) Liquid phase

    Av. temp = 25°C

    Depth of impoundment = 12 ft.

    Volume of surface impoundment in the region of effect of aerators = 12,463 ft^3

    Number of surface aerators = 3 with 20 Hp each

  b) Gas phase

    Av. temp = 25°C

    Impeller diameter = 1 ft

    Impeller rotation = 1000 RPM

    Impeller Hp = 20 Hp

APPENDIX D

Unit Risks Calculated from Ingestion Study Potency Slope

Chemical	Potency Slope 1/(mg/kg/day)	Unit Risk
Aldrin	11.44	3.3×10^{-3}
Benzidine	234.13	6.7×10^{-2}
Carbon Tetrachloride	0.083	2.4×10^{-5}
Chloroform	0.18	5.1×10^{-5}
Chlordane	1.61	4.6×10^{-4}
Chloroalkyl ethers		
BCME	9299.76	2.7
BCEE	1.14	3.3×10^{-4}
Chlorinated benzenes		
HCB	1.68	4.8×10^{-4}
Chlorinated ethanes		
1,2-di-	0.037	1.1×10^{-5}
1,1,2 -tri-	0.057	1.6×10^{-5}
1,1,2,2-tetra-	0.20	5.7×10^{-5}
Hexa	0.014	4×10^{-6}
Chlorinated Phenols		
2,4,6-tri-	0.0199	5.7×10^{-6}
Dichlorobenzidine	1.69	4.8×10^{-4}
DDT	8.42	2.4×10^{-3}
Dichloroethylene		
1,1-dichloroethylene	1.04	3×10^{-4}
Dieldrin	30.37	8.7×10^{-3}
Dinitrotoluene	0.31	8.9×10^{-5}

Chemical	Potency Slope 1/(mg/kg/day)	Unit Risk
Dioxins		
Tetrachlorodioxin	4.25×10^5	121.4
Diphenylhydrazine	0.77	2.2×10^{-4}
Halomethanes	0.18	5.1×10^{-5}
Heptachlor	3.37	9.6×10^{-4}
Hexachlorobutandiene	0.078	2.2×10^{-5}
Hexachlorocyclohexane		
technical grade	4.75	1.4×10^{-3}
alpha isomer	11.12	3.2×10^{-3}
beta isomer	1.84	5.3×10^{-4}
gamma isomer	1.33	3.8×10^{-4}
Nitrosamines		
DMNA	25.88	7.4×10^{-3}
DENA	43.48	1.2×10^{-2}
DBNA	5.43	1.6×10^{-3}
N-nitrosodi-n-propylamine	2.13	6.1×10^{-4}
N-nitrosodiphenylamine	4.92×10^{-3}	1.4×10^{-6}
PAH	11.53	3.3×10^{-3}
PCBs	4.34	1.2×10^{-3}
Toxaphene	1.13	3.2×10^{-4}

APPENDIX E

Multimedia Rate Constants(30),(31)

I.D. Compound	Air Stripping * k_a(1/day)	Biodegradation (Grau Model) $k_{1(s)}X(\frac{\mu g}{L}\frac{1}{day})$	Adsorption on Sludge $K_1(\frac{L}{\mu g})$	$X'(\frac{\mu g}{L})$
1. acenaphthene		6×10^6	0.476	500
2. acrolein		6×10^6	0	
3. acrylonitrile		6×10^6		
4. benzene		3922	0	
5. benzidine		14	0	
6. carbon tetrachloride (tetrachloromethane)		0	0	
7. chlorobenzene		290	0.69	1.36
8. 1,2,4-trichlorobenzene		"	0.69	1.36
9. hexachlorobenzene		"	0.0032	500
10. 1,2-dichloroethane		"	0	
11. 1,1,1-trichloroethane		"	0	
12. hexachloroethane		2.5×10^4	0.69	1.36
13. 1,1-dichloroethane		290	0	
14. 1,1,2-trichloroethane		"	0	

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* The mass transfer coefficients for air stripping can be estimated as described in the main text.

I.D. Compound	Air Stripping $k_a(\frac{1}{day})$	Biodegradation (Grau Model) $k_{1(s)}X(\frac{\mu g}{L}\frac{1}{day})$	Adsorption on Sludge $K_1(\frac{1}{\mu g})$	$X'(\frac{\mu g}{L})$
15. 1,1,2,2-tetrachloroethane		290	0	
16. chloroethane		"	0	
17. bis(chloromethyl) ether	Decomposes in water			
18. bis(2-chloroethyl) ether		$6x10^6$	0	
19. 2-chloroethyl vinyl ether (mixed)		1034	0	
20. 2-chloronaphthalene		40,700	$8.9^{(1)}$	$1.1^{(1)}$
21. 2,4,6-trichlorophenol		290	$0.7^{(1)}$	$1.4^{(1)}$
22. parachlorometa cresol		$2.5x10^6$	0.24	7.1
23. chloroform (trichloromethane)		$2.2x10^6$	0	
24. 2-chlorophenol		$5x10^6$	0.24	7.1
25. 1,2-dichlorobenzene		290	0.69	1.36
26. 1,3-dichlorobenzene		"	0.69	1.36
27. 1,4-dichlorobenzene		"	"	"
28. 3,3-dichlorobenzidine		"	0.0032	500
29. 1,1-dichloroethylene		"	0	

I.D. Compound	Air Stripping	Biodegradation (Grau Model)	Adsorption on Sludge	
	$k_a(\frac{1}{day})$	$k_{1(s)}X\ (\frac{\mu g}{L}\ \frac{1}{day})$	$K_1(\frac{L}{\mu g})$	$X'(\frac{\mu g}{L})$
30. 1,2-trans-dichloroethylene		290	0	
31. 2,4-dichlorophenol		5150	$0.446^{(1)}$	$3.33^{(1)}$
32. 1,2-dichloropropane		"	0	
33. 1,3-dichloropropylene (1,3-dichloropropene)		"	0	
34. 2,4-dimethylphenol		11,250	$0.23^{(1)}$	$13.6^{(1)}$
35. 2,4-dinitrotoluene		386	0.29	20
36. 2,6-dinitrotoluene		"	"	"
37. 1,2-diphenylhydrazine		549	0.0032	500
38. ethylbenzene		652	0	
39. fluroanthene		2.9×10^{-4}	0.476	500
40. 4-chlorophenyl phenyl ether		6×10^{6}	0	
41. 4-bromophenyl phenyl ether		6×10^{6}	0	

I.D. Compound	Air Stripping $k_a(\frac{1}{day})$	Biodegradation (Grau Model) $k_{1(s)}X\ (\frac{\mu g}{L}\ \frac{1}{day})$	Adsorption on Sludge $K_1(\frac{L}{\mu g})$	$X'(\frac{\mu g}{L})$
42. bis(2-chloroisopropyl) ether		$6x10^6$	0	
43. bis(2-chloroethoxy) methane		$6x10^6$	0	
44. methylene chloride (dichloromethane)		$5.3x10^7$	0	
45. methyl chloride (chloromethane)		"	0	
46. methyl bromide (bromomethane)		"	0	
47. bromoform (tribromomethane)		6266	0	
48. dichlorobromomethane		"	0	
49. trichlorofluoromethane		"	0	
50. dichlorodifluro methane		"	0	

I.D. Compound	Air Stripping $k_a(\frac{1}{day})$	Biodegradation (Grau Model) $k_{1(s)}X(\frac{\mu g}{L}\frac{1}{day})$	Adsorption on Sludge $K_1(\frac{L}{\mu g})$	Adsorption on Sludge $X'(\frac{\mu g}{L})$
51. chlorodibromomethane		6266	0	
52. hexachlorobutadiene		$6x10^6$	0.0032	500
53. hexachlorocyclo-pentadiene		"	"	"
54. isophorone		"	0	
55. naphthalene		40,700	8.9	1.1
56. nitrobenzene		2500	0.0015	1000
57. 2-nitrophenol		1810	0.0088	13.3
58. 4-nitrophenol		2500	0.0015	1000
59. 2,4-dinitrophenol		386.4	0.29	20
60. 4,6-dinitro-o-cresol		259	0.29	20
61. N-nitrosodimethylamine		561	0	
62. N-nitrosodiphenylamine		2538	0	
63. N-nitrosodi-n-propylamine		561	0	
64. pentachlorophenol		$2.5x10^4$	0.0032	500
65. phenol		$2.76x10^5$	0.316	33.3

	Air Stripping	Biodegradation (Grau Model)	Adsorption on Sludge	
	$k_a(\frac{1}{day})$	$k_{1(s)}X(\frac{\mu g}{L}\frac{1}{day})$	$K_1(\frac{L}{\mu g})$	$X'(\frac{\mu g}{L})$
66. bis(2-ethylhexyl) phthalate		1685	0	
67. butyl benzyl phthalate		$6x10^6$	0	
68. di-n-butyl phthalate		$6x10^6$	0	
69. di-n-octyl phthalate		2228	0	
70. diethyl phthalate		$6x10^6$	0	
71. dimethyl phthalate		"	0	
72. 1,2-benzanthracene		337	0.476	500
73. benzo (a) pyrene (3,4-benzopyrene)		272	"	"
74. 3,4-benzofluoranthene		"	"	"
75. 11,12-benzofluoranthene		"	"	"
76. chrysene		565	"	"
77. acenaphthene		2865	"	"
78. anthracene		937	0.476	500
79. 1,12-benzoperylene		565	"	"
80. fluorene		1287	"	"
81. phenanthrene		72750	"	"
82. 1,2,5,6-dibenzanthracene		565	"	"

	Air Stripping	Biodegradation (Grau Model)	Adsorption on Sludge	
	$k_a(\frac{1}{day})$	$k_{1(s)}X(\frac{\mu g}{L}\frac{1}{day})$	$K_1(\frac{L}{\mu g})$	$X'(\frac{\mu g}{L})$
83. indeno (1,2,3-C,D) pyrene		272	5.58	20.8
84. pyrene		"	5.58	20.8
85. tetrachloroethylene		290	0	0
86. toluene		39000	0	0
87. trichloroethylene		263	0	
88. vinyl chloride		1240	0	
89. aldrin		400	1.1	200
90. dieldrin		"	"	"
91. chlordane		"	"	"
92. DDT		"	"	"
93. DDE		"	"	"
94. DDD		"	"	"
95. Endosulfan-alpha		"	"	"
96. Endosulfan-beta		"	"	"
97. Endosulfan sulfate		"	"	"

	Air Stripping $k_a(\frac{1}{day})$	Biodegradation (Grau Model) $k_{1(s)}X(\frac{\mu g}{L}\frac{1}{day})$	Adsorption on Sludge $K_1(\frac{L}{\mu g})$	 $X'(\frac{\mu g}{L})$
98. endrin		400	1.1	200
99. endrin aldehyde		"	"	"
100. heptachlor		"	"	"
101. heptachlor epoxide		"	"	"
102. BHC-alpha		"	"	"
103. BHC-beta		"	"	"
104. BHC-gamma		"	1.1	200
105. BHC-delta		"	"	"
106. PCB-1242		454	"	"
107. PCB-1254		400.6	"	"
108. PCB-1221		10000	"	"
109. PCB-1232		10000	"	"
110. PCB-1248		$9.5\text{x}10^{-10}$	"	"
111. PCB-1260		116	"	"
112. PCB-1016		599	"	"
113. toxaphene		400	"	"

	Air Stripping $k_a(\frac{1}{day})$	Biodegradation (Grau Model) $k_{1(s)}X(\frac{\mu g}{L}\frac{1}{day})$	Adsorption on Sludge $K_1(\frac{L}{\mu g})$	 $X'(\frac{\mu g}{L})$
114. antimony		0	0.0568	454.5
115. arsenic		"	0.024	153.8
116. asbestos				
117. beryllium		0	1.88	3.33
118. cadmium		"	11.3	2.2
119. chromium		"	0.0085	10000
120. copper		"	0.23	10000
121. cyanides			125	263
122. lead		0	0.0465	500
123. mercury		0	4.55	20
124. nickel		0	0.0326	66.7
125. selenium		0	0.97	11.1
126. silver		0	0.238	100
127. thallium		"	0.4	50
128. zinc		"	0.0096	50000
129. 2,3,7,8-tetrachloro dibenzo-p-dioxin		290	0.0032	500

APPENDIX F

$$Q_i = K_L \ (\text{in } \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}) \ x_i \cdot A \cdot MW_i \qquad \text{(F-1)}$$

$$= K_L \ (\text{in 1/sec}) \ C_{Li} \cdot V \qquad \text{(F-2)}$$

$$= K_L \ (\text{in cm/sec}) \ C_{Li} \cdot A \qquad \text{(F-3)}$$

where Q_i : emission rate of component i, gr/sec

x_i : mole fraction of component i

A : surface area of an impoundment, cm^2

MW_i : molecular weight of component i

V : volume of a surface impoundment ($= A \cdot D$), cm^3

D : depth, cm

C_{Li} : concentration of component i, gr/cm^3

Since

$$x_i = C_{Li} \frac{1}{\rho_M} \frac{MW_M}{MW_i} \qquad \text{(F-4)}$$

where MW_M is the molecular weight of mixture, and ρ_M is the density of the mixture, gr/cm^3, one gets from Equations (F-1), (F-2), and (F-4)

$$K_L \ (\text{in 1/sec}) = K_L \ (\text{in } \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}) \ \frac{MW_M}{D \cdot \rho_M} \qquad \text{(F-5)}$$

Also from Equations (F-1), (F-3), and (F-4)

$$K_L \ (\text{in cm/sec}) = K_L \ (\text{in } \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}) \ \frac{MW_M}{\rho_M}$$

If the mixture is aqueous solution in which sparingly soluble compounds are dissolved, MW_M corresponds to the molecular weight of water.

PART B - EMISSION MONITORING AND MEASUREMENTS

I. Ambient Air Monitoring

1) Analytical Protocol for Organic Compounds

1.0 Principle of Method

Recovery of volatile organics from Tenax GC is accomplished by thermal desorption and purging with helium into a liquid nitrogen cooled nickel capillary trap and then the vapors are introduced into a high resolution glass gas chromatographic column where the constituents are separated from each other. Characterization and quantification of the constituents in the sample are accomplished by mass spectrometry either by measuring the intensity of the total ion current signal or by extracted ion current profile. The analysis is shown in Figure 1.

2.0 Range and Limits of Detection

The linear range for the analysis of volatile compounds depends upon two principal features. The first is a function of the breakthrough volume of each specific compound which is trapped on the Tenax GC sampling cartridge and the second is related to the inherent limits of detection of the mass spectrometer for each organic. Thus, the range and the maximum limit of detection are a direct function of each compound which is present in the original ambient air. The linear range for quantitation using glass capillaries on a gas chromatograph/mass spectrometer/computer (GC/MS/COMP) is generally three orders of magnitude [5-5,000ng]. Table 1 lists the overall detection limits for some examples of volatile organics which are based on these two principles.

TABLE 2. PAINT FACTORS FOR FIXED ROOF TANKS

Tank color		Paint factors (F_p)	
		Paint condition	
Roof	Shell	Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminium (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44[a]
Medium gray	Medium gray	1.40	1.58[a]

[a] Estimated from the ratios of the seven preceding paint factors.

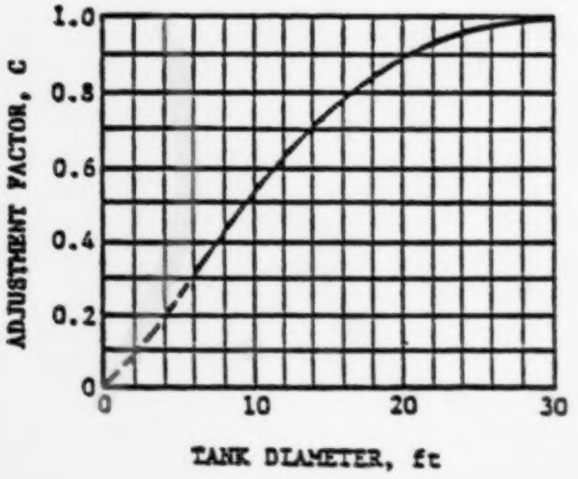

Figure 1. Adjustment factor (C) for small diameter tanks.

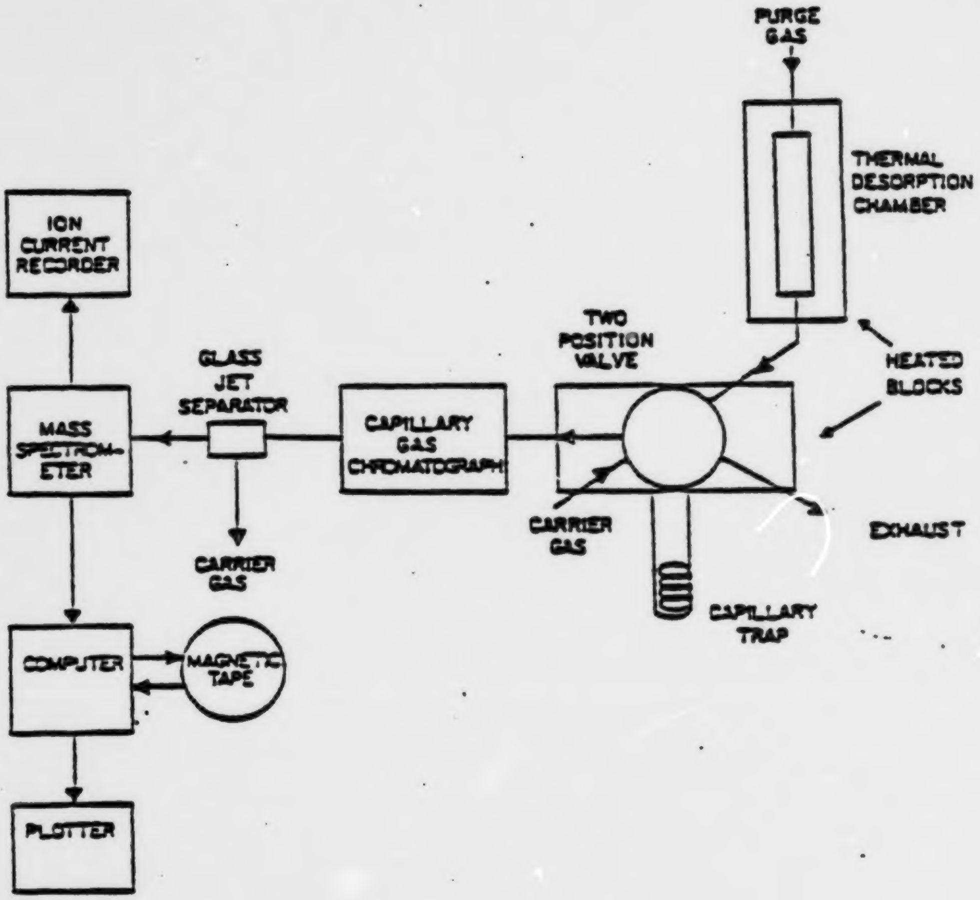
PURGE GAS
THERMAL DESORPTION CHAMBER
ION CURRENT RECORDER
TWO POSITION VALVE
HEATED BLOCKS
GLASS JET SEPARATOR
MASS SPECTROM-ETER
CAPILLARY GAS CHROMATOGRAPH
CARRIER GAS
EXHAUST
CARRIER GAS
CAPILLARY TRAP
COMPUTER
MAGNETIC TAPE
PLOTTER

Figure 1. Analytical system for analysis of organic vapors in ambient air.

Table 1. APPROXIMATE MEASURED LIMITS OF DETECTION AND QUANTIFIABLE LIMITS FOR SELECTED VAPOR-PHASE ORGANICS IN AMBIENT AIR

Compound	*m/z*	LOD[a]		QL	
		$\mu g/m^3$	ppt	$\mu g/m^3$	ppt
Benzene	78	0.08	26	0.40	128
Chloroform	83/85	0.08	17	0.40	85
1,2-Dichloroethane	98/62	0.12	31	0.60	153
1,1,1-Trichloroethane	97/99	0.16	31	0.80	154
Carbon tetrachloride	117/119	0.24	39	1.20	195
Vinylidene chloride	96/98	0.12	31	0.60	156
Trichloroethylene	130/132	0.16	31	0.80	154
Tetrachloroethylene	164/166	0.24	36	1.20	179
Bromodichloromethane	127/83	0.24	37	1.20	184
Chlorobenzene	112/114	0.16	36	0.80	179
1,1,2-Trichloroethane	97/99	0.16	31	0.80	154
m-Dichlorobenzene	146/148	0.20	34	1.00	169

[a] Limit of Detection (LOD) was defined as S/N = 4 for *m/z* ion selected for quantification. Quantification Limit (QL) was defined as 5 x LOD or S/N = 20. Limits are based on a collection volume of 25 ℓ or breakthrough volume (70°F), which ever is smaller, for 1.5 cm x 8.0 cm Tenax GC bed volume and mass spectrometer response to that compound.

3.0 Interferences

For the target compounds in Table 1, no interferences have been observed. Particular attention must be paid to the preparation of clean collection devices and the use of apropriate blanks and controls to establish that the background contaminants have been removed. Otherwise, false positive detection of chloroform, toluene, or benzene may occur.

Precautions must be taken for sampling caustic atmospheres which contain levels of NO_x and molecular halogens greater than 2-5 ppm and 25 ppb, respectively. Quenching agents incorporated into the particulate filter should be employed in these cases.

4.0 Precision and Accuracy

The reproducibility of this method has been determined to ±10 to ±30% of the relative standard deviation for different substances when replicate sampling cartridges are examined. The inherent analytical errors are a function of several factors: (1) the ability to accurately determine the breakthrough volume and its relation to field sampling conditions for each of the organic compounds identified; (2) the accurate measurement of the ambient air volume sampled; (3) the percent recovery of the organic from the sampling cartridge after a period of storage; (4) the reproducibility of thermal desorption for a compound from the cartridge and its introduction into the analytical system; (5) the accuracy of determining the relative molar response ratios between the identified substance and the external standard used for calibrating the analytical system; (6) the reproducibility of transmitting the sample through the high resolution gas chromatographic column; and (7) the day-to-day reliability of the MS/COMP system.

The accuracy of analysis is generally +10-30% but depends on the chemical and physical nature of the compound.

5.0 Apparatus and Reagents

5.1 Collection and Analysis Devices

5.1.1 Personal Monitor Pump

A personal monitor pump (MSA Co. - Model C-200) is used for sample collection. Flow rates are adjusted to 0.05 /min for an 8 hour collection period. Flows are adjusted such that a total volume of 0.025 m^3 air is sampled for a given collection period.

5.1.2 Sampling Cartridges

The sampling tubes are prepared by packing a ten centimeter long by 1.5 cm i.d. glass tube containing 8 cm of 35/60 mesh Tenax GC with glass wool in the ends to provide support. Virgin Tenax (or material to be recycled) is extracted in a Soxhlet apparatus for a minimum of 18 hours each time with methanol and n-pentane prior to preparation of cartridge samplers.

After purification of the Tenax GC sorbent and drying in a vacumn oven at 120°C for 3 to 5 hours at 28 inches of water, all the sorbent material is meshed to provide a 35/60 particle size range. Meshing and all further cartridge preparation is conducted in a "clean" room. Cartridge samplers are then prepared and conditioned at 270°C with a purified helium flow of 30 ml/min for 120 min. Prior to entering the Tenax GC cartridge the helium is purified by passing through a liquid N_2 cooled cryogenic trap. The conditioned cartridges are transferred to Kimax (2.5 x 150 cm) culture tubes, immediately sealed using Teflon-lined caps and cooled. This procedure is performed in order to avoid recontamination of the sorbent bed.

5.1.3 Inlet Manifold

An inlet manifold for thermally recovering vapors trapped on Tenax sampling cartridges is used and is shown in Figure 1.

5.1.4 Gas Chromatograph

A Varian 1700 or a Pye Unicam 102 gas chromatograph is used to house the glass capillary column and is interfaced to the inlet manifold on the Varian MAT CH-7 or LKB 2091 systems, respectively. A mass flow controller (Tylan) is used to precisely control the carrier gas. Such an analytical system was presented schematically in Figure 1.

A jet separator is employed to interface the glass capillary column to the mass spectormeter on the Varian MAT CH-7 GC/MS/COMP or LKB 2091 systems. The separator is maintained at 240°C.

5.1.5 Mass Spectrometer/Computer

A Varian MAT CH-7 or KLB 2091 mass spectrometer capable of a resolution of 1500-2,000 equipped with single ion monitoring capability is used in tandem with the Varian 1700 or Pye Unicam 102 gas chromatograph and interfaced to a Varian 620/L or PDP 11/04 computer, respectively (Figure 1).

5.2 Reagents and Materials

All reagents used are analytical reagent grade. All solvents (Burdick & Jackson) are redistilled before their use.

6.0 Procedure

6.1 Cleaning of Glassware

All glassware is washed in Isoclean/water, rinsed with dionized distilled water, acetone and air dried. Glassware is heated to 450-500°C for 2 hours to insure that all organic material has been removed prior to its use.

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6.2 Collection of Volatile Organics in Ambient Air

For large sample volumes, it is important to realize that the total volume of air may cause the elution of compounds through the sampling tube if their breakthrough volume is exceeded. The breakthrough volumes of some of the volatile organics are shown in Table 2. These breakthrough volumes have been determined and verified by previously described techniques.

The breakthrough volume is defined as that point at which 50% of a discrete sample introduced into the cartridge is lost. Although the identity of a compound during ambient air sampling is not known (therefore, also its breakthrough volume), the compound can still be quantified after identification by GC/MS/COMP once the breakthrough volume has subsequently been established. Thus, for calculating concentration, the last portion of the sampling period which represents the volume of air sampled prior to breakthrough is selected. For cases in which the identity of a volatile organic compound is not known until after GC/MS, the breakthrough volume is subsequently determined.

Previous experiments have shown that the organic vapors collected on Tenax GC sorbent are stable and can be quantitatively recovered from the cartridge samplers up to 4 weeks after sampling when they are tightly closed in cartridge holders and placed in a second container that can be sealed, protected from light and stored at -20°C (Table 3).

6.2.1 Deuterated Standards

The use of deuterated compounds provides for an assessment of any premature breakthrough (and thus reduced collection efficiency) which may occur if the total vapor-phase organic load exceeds 1/10

Table 2. TENAX GC BREAKTHROUGH VOLUMES FOR TARGET COMPOUNDS[a]

Compound	b.p. (°C)	Temperature (°F)					
		50	60	70	80	90	100
chloroform	61	56	41	32	24	17	13
carbon tetrachloride	77	45	36	28	21	17	13
1,2-dichloroethane	83	71	55	41	31	24	19
1,1,1-trichloroethane	75	31	24	20	16	12	9
tetrachloroethylene	121	481	356	261	192	141	104
trichloroethylene	87	120	89	67	51	37	28
chlorobenzene	132	1989	871	631	459	332	241

[a] For a Tenax GC bed of 1.5 x 8.0 cm.

Table 3. RECOVERY OF TARGET COMPOUNDS AFTER STORAGE

Compound	1 day	1 wk	2 wk
Benzene	100	107 ± 26	69 ± 8
Chloroform	100	83 ± 14	49 ± 4
1,2-Dichloroethane	100	100 ± 5	100 ± 7
1,1,1-Trichloroethane	100	87 ± 17	71 ± 7
Carbon tetrachloride	ND	ND	ND
Vinylidene chloride	100	92	ND
Trichloroethylene	100	87 ± 17	71 ± 7
Tetrachloroethylene	100	92 ± 1	78 ± 4
Bromodichloromethane	ND	ND	ND
Chlorobenzene	100	87 ± 3	80 ± 7
1,1,2-Trichloroethane	100	95 ± 3	92 ± 2
m-Dichlorobenzene	100	89 ± 15	85 ± 3

of the cartridge capacity during field sampling. d_5-Bromoethane (B.P. 80), d_8-tetrahydrofuran (B.P. 65), d_6-benzene (B.P. 80), d_{10}-cyclohexene (B.P. 83) and d_5-chlorobenzene (B.P. 132) are loaded as a discrete zone onto at least 10% of all Tenax GC sampling cartridges prior to sampling. Using GC/MS/COMP the exogenous deuterated compounds are differentiated from the endogenous vapor-phase organics in ambient air.

The addition of these deuterated standards is performed by injecting 1.0 ml air/vapor of the substances onto the "front" end of the cartridge. An air/vapor mixture stream containing 200-400 ng/ml is generated using permeation tubes of each compound with a permeation system.

The quantity of each substance on the sampling cartridges is determined by GC/MS/COMP after field sampling and the percent recovery is compared to control (unused) cartridges carried to and from the field sampling site and subjected to the same storage regime. Statistically significant differences are attributed to premature breakthrough.

6.2.2 Quantification Standards

Unique substances may be added as internal standards during sampling. Examples are the deuterated compound listed under 6.2.1. However, the volume of air sampled is accurately known and thus external standards may be introduced into the cartridge prior to its analysis. Three standards, hexaflourobenzene, octafluorotoluene, and iodotoluene are used for the purpose of calculating RMRs and the levels in ambient air. Previous research has shown that their retention times span the chromatographic range of analysis (SE-30 coatead capillary) and they do not interfere with the analysis of unknown compounds in ambient air samples.

The external standards (300-400 ng) are injected into the sampling cartridges as a 1.0 ml air/vapor mixture using a gas sampling syringe. The air/vapor mixture is synthesized using permeation tubes and a permeation system.

6.3 Analysis of Samples

The instrumental conditions for the analysis of volatile organics on the sorbent Tenax GC sampling cartridge is shown in Table 4. The thermal desorption chamber and the six port Valco valve are maintained at 270°C. The jet separator is maintained at 245°. The mass spectrometer is set to scan the mass range from approximately 20-350. The helium purge gas though the desorption chamber is adjusted to 15-20 mL/min. The nickel capillary trap on the inlet manifold is cooled with liquid nitrogen. In a typical thermal desorption chamber and the helium gas is channeled through the cartridge to purge vapors into the liquid nitrogen capillary trap (the inert activity efficiency of the trap has been shown in a previous study). After the desorption has been completed, the six-port valve is rotated and the temperature on the capillary loop is rapidly raised (greater than 10°/min); the carrier gas then introduces the vapors onto the high resolution GC to 240°C at 4°C/min and held at the upper limit for a minimum of 10 min. After all the components have eluted the column is then cooled to ambient temperature and the next sample is processed.

6.3.1 Qualitative Analysis

The mass spectral data are processed in the following manner. First, the original spectra are scanned and the reconstructed ion

Table 4. OPERATING PARAMETERS FOR GLC-MS-COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber and valve	270°C
capillary trap - minimum	-195°C
maximum	240°C
thermal desorption time	8 min
He purge flow .	15 ml/min
GLC	
85 m glass WCOT $BaCO_3$ SE-30 (0.8-1.0 μ film)	24-240°C, 4°C/min
carrier (He) flow	~1.25 ml/min
separator/transfer line	245°C
MS	
Varian MAT CH-7	
scan range	m/z 20 → 350
scan cycle, automatic-cyclic	1 sec/decade
filament current	300 μA
multiplier	4.0
ion source vacuum	~4 x 10^{-6} T
LKB 2091	
scan range	m/z 20 → 500
scan cycle, automatic	2 sec total
filament current	300 μA
multiplier	4.5
ion source vacuum	~4 x 10^{-6} T

chromatogram (RIC) is extracted and examined. The intensity (RIC) is plotted against the spectum number using the software package available. The information will generally indicate whether the run is suitable for further processing, since it provides some idea of the number of unknowns in the sample and the resolution obtained using the particular gc column conditions.

If mass conversion of spectral peak times to peak masses has not been performed on-the-fly during the data acquisition by hardware methods then this function is next performed by software methods (magnetic systems). In either case the mass conversion is accomplished by the use of the calibration table obtained prior to sample analysis for perfluorokerosene. In general the calibration data are sufficient for an entire day's data processing; however, it is verified every eight hours.

After the spectra are obtained in mass converted form, processing proceeds either manually or by computer by comparison to a Library. Compound identification can involve various degrees of certainty. These levels of identification have been defined as follows:

Level I Computer Interpretation. The raw data generated from the analysis of samples are subjected to computerized deconvolution/library search and compoud identification made using this approach has the lowest level of confidence. In general Level I is reserved for only those cases where compound verification is the primary intent of the qualitative analysis.

Level II Manual Interpretation. The plotted mass spectra are manually interpreted by a skilled interpretor and compared to those spectra compiled in a data compendium.

In general a minimum of five masses and intensities (±5% S.D.) should match between the unknown and library spectrum. This level does not utilize any further information such as retention time since many compounds the authentic compounds may not be available for establishing retention times.

Level III Manual Interpretation Plus Retention Time/Boiling Point of Compound. In addition to the effort as described under Level II, the retention time of the compound is compared to the retention time which has been derived from previous chromatographic analysis. Also the boiling point of the identified compound is compared to the boiling points of other compounds in the near vicinity of the one in question when a capillary coated with a non-polar phase has been used.

Level IV Manual Interpretation Plus Retention Time of Authentic Compounds. Under this level, the authentic compound has been chromatographed on the same capillary column using identical operating conditions and the mass spectrum of the authentic compound is compared to that of the unknown.

Level V Level IV Plus Independent Confirmation Techniques. This level utilizes other physical methods of analysis such as GC/fourier transform/IR, GC/high resolution mass spectrometry, or NMR analysis. This level constitutes the highest degree of confidence in the identification of organic compounds.

The application rate = 1.5 #/ft², or

$$\frac{M_T}{A} = 1.5 \times \frac{454}{30.48^2} = 0.733 \text{ gr/cm}^2$$

The total depth of penetration

$$h_p = h_s + \text{depth of penetration} = 12.7 + 12.7 = 25.4 \text{ cm}$$

The mass fraction oil in the film form (Equation (63))

$$w_f = \frac{0.5}{h_p \quad \rho_B} \left(\frac{M_T}{A}\right) = \frac{0.5}{(25.4)(0.8)} \quad (0.733)$$

$$= 0.018$$

From Equation (59), the oil film thickness on soil is (use d_p = 0.005 cm)

$$z_o = 0.005 \frac{(2.65)(0.018)}{6(0.9)} = 0.000044 \text{ cm}$$

From Equation (60) the diffusion path length for the lump is

$$z_o = 0.005/2 = 0.0025 \text{ cm}$$

The vapor pressure of benzene at 25°C is 95 mmHg. If the activity coefficient of benzene in oil is assumed to be unity for a total pressure of 760 mmHg, the vapor liquid equilibrium constant K = 0.125 (See Eq. (A-5) in the appendix). Using Equation (A-8) in the appendix, one gets

$$H_c = \frac{0.125}{2.44 \times 10^4} \quad \frac{200}{0.9} = 1.14 \times 10^{-3}$$

Also

D_{wi} for benzene in oil = 1×10^{-7} cm²/sec ($D_{wi} \propto \frac{1}{\mu}$; $D_{wi} = 10^{-5}$ @ μ=1cp)

$D_{ei} = D_i \; \epsilon^{4/3}$ (recommended by Thibodeaux (26))

$0.088 \times (0.35)^{4/3} = 0.022$ cm²/sec

a_s for film (Equation (61)) = 6/0.005 = 1200 cm²/cm³

a_s for lump (Equation (62)) = 2.7/0.005 = 540 cm²/cm³

Substitution of these values into Equation (56) yields

$$C_{ig} \text{ for film} = \left[\frac{1.14 \times 10^{-3}}{1+1.14\times10^{-3} \, \dfrac{6(0.022)(0.000044)}{1\times10^{-5}\,(1200)(645)}} \right] (1.35\times10^{-3})$$

$$= 1.54\times10^{-6} \text{ gr/cm}^3$$

where

$$h_p^2 + h_p\,h_s - 2\,h_s^2 = 25.4^2 + (25.4)(12.7) - 2(12.7)^2 = 645 \text{ cm}^2$$

$$C_{ig} \text{ for lump} = \left[\frac{1.14 \times 10^{-3}}{1+1.14\times10^{-3} \, \dfrac{6(0.022)(0.0025)}{1\times10^{-7}\,(540)(645)}} \right] (1.35\times10^{-3})$$

$$= 1.54 \times 10^{-6} \text{ gr/cm}^3$$

$\frac{m_{io}}{A}$ (wt. of benzene applied per unit area of landfarm)

$$= 0.733 \times \frac{1500}{10^6} = 1.1 \times 10^{-3} \text{ gr/cm}^3$$

The dry-out time is calculated using Equation (58)

$$t_d \text{ for film} = \frac{25.4 + 12.7}{2(0.022)(1.54\times10^{-6})}(1.1\times10^{-3})(0.5) = 3.1\times10^5 \text{ sec}$$

(3.6 days)

$$t_d \text{ for lump} = \frac{38.1}{2(0.022)(1.54\times10^{-6})}(1.1\times10^{-3})(0.5) = 3.1\times10^5 \text{ sec}$$

In this case the dry-out times for both film and oil lump are the same. From Equation (55) the average emission rate during the period of the dry-out time is

$$\bar{Q}_i \text{ for film} = \frac{2(0.022)(1.54\times10^{-6})(4047\times10^{4})}{\left[12.7^2 + \frac{2(0.022)(3.1\times10^{5})(12.7)(1.54\times10^{-6})}{1.1\times10^{-3}(0.5)}\right]^{1/2}}$$

$$= 0.11 \text{ gr/sec}$$

$\bar{Q}_i$ for lump = 0.11 gr/sec

The average emission rate is

0.11 + 0.11 = 0.22 gr/sec

VI. Dispersion Modeling-Screening Technique

A disposal facility (1/2 acre) is emitting volatile hazardous chemicals at the following rates:

Compound	Emission Rate (gr/sec)
benzene	0.17
trichloroethylene	0.034
ethylene dichloride	0.18

Evaluate the impact of the facility on ambient air quality.

In order to utilize the screening technique for estimating the impact, the following data are obtained from the permit applicant:

Distance from the facility to the downwind public: L=1000 m

Frequency that wind blows from the sector of interest: $\phi=0.25$

Average annual temperature: 25°C

Stability Class: D

Annual average wind speed: 5 m/sec

At L = 1000 m and D stability, $\sigma_z = 32$ m.

Distance from virtual point to the disposal facility (Equation (47))

$$L' = \frac{(0.5\times4047\times10^{4})}{2}^{0.5} \cdot \cot\left(\frac{22.5}{2}\right) = 11300 \text{ cm (113m)}$$

The width of the facility

$$S = (0.5 \times 4047 \times 10^4)^{0.5}$$

$$= 4500 \text{ cm } (45\text{m})$$

Since $S < 400$ m, the screening technique can be used. The virtual downwind distance is

$$L_v = 113 + 1000 = 1113 \text{ m}$$

The net downwind concentration is obtained from Equation (65)

1) benzene

$$\chi = \frac{16}{2\pi(1113)} \quad \frac{2(0.17)}{\sqrt{2\pi} \quad (32)(5)} \quad (0.25) = 4.9\times10^{-7} \text{ gr/m}^3$$

$(= 0.49\ \mu\text{gr/m}^3)$

2) trichlorobenzene

$\chi = 1\times10^{-7}$ gr/m^3 (0.1 μgr/m^3)

3) ethylene dichloride

$\chi = 5.1\times10^{-7}$ gr/m^3 (0.51 μgr/m^3)

The background concentration of each compound should be added to the results above to obtain the downwind concentrations. The estimated annual average of the downwind concentration would be higher than the net concentration given above if the background concentration is taken into account.

At an assumed lifetime cancer risk of 10^{-5} the maximum ambient levels of each compound not allowed to exceed are obtained from Equation (67)

1) Benzene

$$C_{mi} = \frac{10^{-5}}{4.8\times10^{-5}} = 0.21\ \mu\text{gr/m}^3$$

2) trichloroethylene

$$C_{mi} = \frac{10^{-5}}{4.2\times10^{-6}} = 2.4\ \mu\text{gr/m}^3$$

3) ethylene dichloride

$$C_{mi} = \frac{10^{-5}}{1.2\times10^{-5}} = 0.83\ \mu gr/m^3$$

To account for the additive health effect of carcinogens, the sum of normalized permissible maximum concentrations (SNPMC) is determined

$$\text{SNPMC} = \frac{0.49}{0.21} + \frac{0.1}{2.4} + \frac{0.51}{0.83} = 2.99$$

The maximum allowable downwind concentrations of each compound at 10^{-5} risk are now:

1) benzene

$$\frac{0.21}{2.99} = 0.07\ \mu gr/m^3$$

2) trichloroethylene $0.1\ \mu gr/m^3$

3) ethylene dichloride $0.51\ \mu gr/m^3$

In order to meet these concentrations, the emission rates of benzene from the disposal facility should be reduced to

$$0.17 \times \frac{0.07}{0.49} = 0.024\ gr/sec$$

Or other adjustments on the emission rate of each component can be made to meet SNPMC $\lesssim 1$. For example, if the allowable downwind concentration of benzene is doubled while that of ethylene dichloride is reduced by a factor 2, the allowable concentration should be

1) benzene $0.14\ \mu gr/m^3$

2) trichloroethylene $0.1\ \mu gr/m^3$

3) ethylene dichloride $0.25\ \mu gr/m^3$

$$\text{SNPMC} = \frac{0.14}{0.21} + \frac{0.1}{2.4} + \frac{0.25}{0.83} \cong 1$$

Hence the emission rate of each compound should not exceed

1) benzene $0.17\times \frac{0.14}{0.49} = 0.05\ gr/sec$

2) trichlorobenzene 0.034 gr/sec

3) ethylene dichloride $0.18 \times \frac{0.25}{0.51} = 0.09$ gr/sec

VII. Consideration of Other Health Criteria

Ambient air monitors are installed to monitor the effect of a treatment facility on the ambient air concentration of cyanides. The treatment facility is a 0.25 acre agitated lagoon. The average concentration of cyanides in the form of hydrogen cyanide in the lagoon is about 2000 mg/L. Estimate the impact of the facility on the downwind monitor when the average velocity is 5 m/s (stability class = D). Additional information obtained is:

. Background cyanide concentration in the ambient air = 0.1 μgr/m^3.
Distance of lagoon to the downwind monitor = 200 m.
Effective zone of turbulence = 5%.
Average temperature = 25°C.

Calculations similar to Example 1 can be used to estimate the overall mass transfer coefficient (MW of HCN = 27).

i) Convective zone

a) Liquid phase

$$k_{L,i} = \left(\frac{32}{27}\right)^{0.5} \times 1.23 \times 10^{-4} = 1.34 \times 10^{-4} \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

b) Gas phase

$$k_{g,i} = \left(\frac{18}{27}\right)^{0.335} \times 5.8 \times 10^{-5} = 5.06 \times 10^{-5} \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

ii) Agitated zone

a) Liquid phase

$$k_{L,i} = \left(\frac{32}{27}\right)^{0.25} (0.13) = 0.136 \frac{\text{gr-mol}}{\text{cm}^2 \cdot \text{sec}}$$

b) Gas phase

$$k_{g,i} = \left(\frac{18}{27}\right)^{0.25} \times 9.5\times10^{-4} = 8.58 \times10^{-4} \ \frac{\text{gr-mol}}{\text{cm}^2\cdot\text{sec}}$$

The vapor-liquid equilibrium constant, K_i, for HCN in aqueous solution is estimated by

$$K_i = \frac{\gamma_i \ P_i^o}{P}$$

The vapor pressure of HCN at 25°C = 735 mmHg from a handbook, and $\gamma_i \cong 1$ will be used for the dilute concentration.

$$K_i = \frac{(1)\ (735)}{760} = 0.967$$

The overall liquid phase mass transfer coefficients in the convective ($(K_L)_c$) and turbulent ($(K_L)_T$) zones are obtained from Equation (2)

$$\frac{1}{(K_L)_c} = \frac{1}{1.34 \times 10^{-4}} + \frac{1}{0.967 \times 5.06\times10^{-5}} = 2.79 \times 10^4$$

$$(K_L)_c = 3.6 \times 10^{-5} \ \frac{\text{gr-mol}}{\text{cm}^2\cdot\text{sec}}$$

$$\frac{1}{(K_L)_T} = \frac{1}{0.136} + \frac{1}{0.967 \times 8.58 \times 10^{-4}} = 1.21 \times 10^3$$

$$(K_L)_T = 8.25 \times 10^{-4} \ \frac{\text{gr-mol}}{\text{cm}^2\cdot\text{sec}}$$

The average mass transfer coefficient for the entire lagoon is obtained as follows:

$$K_L = 3.6 \times 10^{-5}\ (0.95) + 8.25 \times 10^{-4}\ (0.05)$$

$$= 7.5 \times 10^{-5} \ \frac{\text{gr-mol}}{\text{cm}^2\cdot\text{sec}}$$

The concentration of HCN in the aqueous solution is converted to mole fraction,

$$x_i = \frac{2000}{10^6} \times \frac{1/27}{1/18} = 1.33 \times 10^{-3} \text{ mole fraction}$$

The emission rate of HCN from the treatment lagoon is estimated from Equation (3)

$$Q_i = 27(\ 7.5 \times 10^{-5})(0.25 \times 4047 \times 10^4)(1.33 \times 10^{-3})$$

$$= 27.2 \text{ gr/sec}$$

Dispersion modeling will be used to estimate the impact on the downwind monitoring. As in Example V , the width of the facility is

$$S = (0.25 \times 4047 \times 10^4)^{0.5} = 3180 \text{ cm } (31.8 \text{ m})$$

Since S < 80 m where 80 m is 40% of the 200 m, the screening technique can be used. The distance from virtual point to the disposal facility is

$$L' = \frac{31.8}{2}(5.03) = 80 \text{ m}$$

The virtual downwind distance is

$$L_v = 80 + 200 = 280 \text{ m}$$

The net concentration impacting the downwind monitor is (Equation (65)).

$$\chi = \frac{16}{2\pi\ (280)}\ \frac{2\ (20.9)}{\sqrt{2\pi}\ (8.5)(5)}(1) = 3.57 \text{ x}10^{-3}\ \frac{\text{gr}}{\text{m}^3}\ \left(= 3570\ \frac{\mu\text{gr}}{\text{m}^3}\right)$$

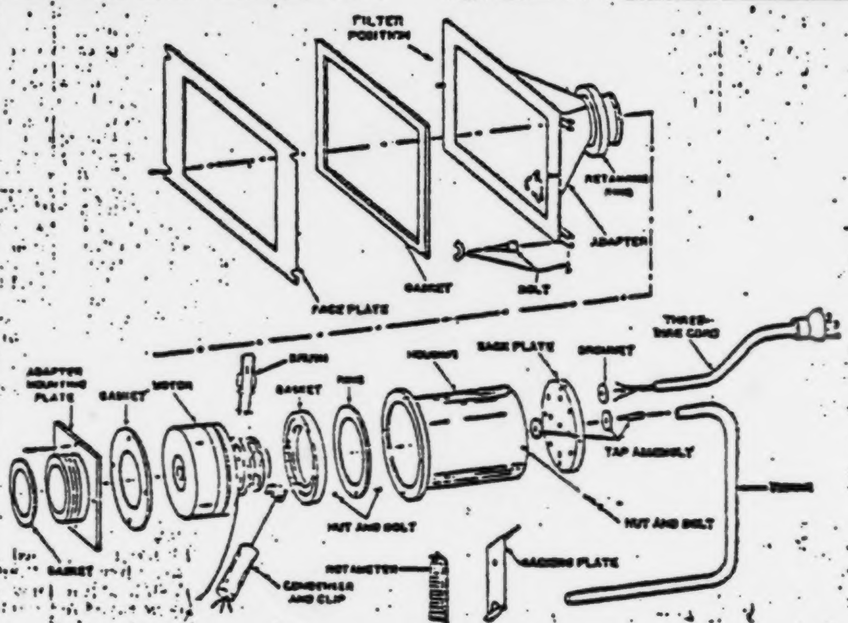
2) High Volume Sampler for Measurement of Trace Elements Suspended in Ambient Air.

The suspended particulates in the ambient air are collected on filter papers using the High Volume Sampler. The detail chemical analysis on the collected particulates can be performed for quantification of hazardous constituents in the particulates. The method for operation, maintenance, and calibration of the High Volume Sampler can be found in the Federal Register publication, Vol. 36, 22388 November 25, 1971. The content of the reference method is summarized in the Appendix of Part B for information.

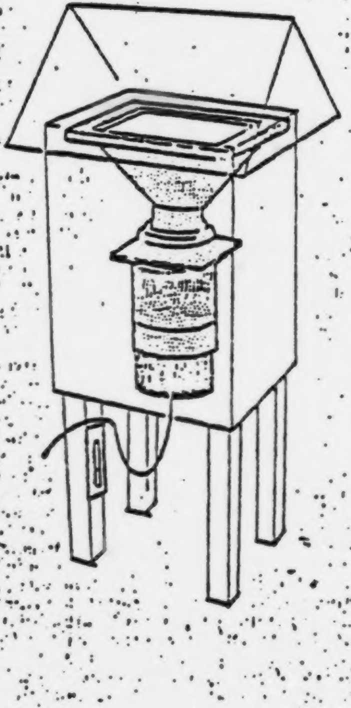
PART B - Appendix
High Volume Sampler

Sampler - The sampler consists of three units (1) the faceplate and gasket, (2) the filter adapter assembly, and (3) the motor unit. Figure 1 shows an exploded view of these parts, their relationship to each other, and how they are assembled. The sampler must be capable of passing environmental air through a 406.5 cm^2 (63 in.^{2}) portion of a clean 20.3 by 25.4 cm. (8- by 10- in.) glass-fiber filter at a rate of at least 1.70 m^3/min. (60 ft.^{3}/min.). The motor must be capable of continuous operation for 24-hour periods with input voltages ranging from 110 to 120 volts, 50-60 cycles alternating current and must have third-wire safety ground. The housing for the motor unit may be of any convenient construction so long as the unit remains airtight and leakfree. The life of the sampler motor can be extended by lowering the voltage by about 10 percent with a small "buck or boost" transformer between the sampler and power outlet.

Sampler Shelter - It is important that the sampler be properly installed in a suitable shelter. The shelter is subjected to extremes of temperature, humidity, and all types of air pollutants. For these reasons the materials of the shelter must be chosen carefully. Properly painted exterior plywood or heavy gauge aluminum serve well. The sampler must be mounted vertically in the shelter so that the glass-fiber filter is parallel with the ground. The shelter must be provided with a roof so that the filter is protected from precipitation and debris. The internal arrangement and configuration of a suitable shelter with a gable roof are shown in


FILTER POSITION
RETAINING RING
ADAPTER
GASKET
BOLT
FACE PLATE
THREE-WIRE CORD
ADAPTER MOUNTING PLATE
GASKET
MOTOR
BRUSH
GASKET
RING
HOUSING
BASE PLATE
GROMMET
TAP ASSEMBLY
TUBING
NUT AND BOLT
NUT AND BOLT
GASKET
CONDENSER AND CLIP
ROTAMETER
BACKING PLATE

[redacted]. Exploded view of typical high-volume air sampler parts.



Assembled sampler and shelter.

FIGURE I

Figure I. The clearance area between the main housing and the roof at its closest point should be 580.5 ± 193.5 cm^2 (90 ± 30 in.^{2}). The main housing should be rectangular, with dimensions of about 29 by 36 cm. (11 1/2 by 14 in.). Note: The use of the motor assembly as a sampler without a shelter similar to that pictured in Figure I is unacceptable.

Flow Device - A pressure transducer and recorder is the preferred method of flow measurement, a rotameter capable of being calibrated is also an acceptable method.

Filter Media - Glass-fiber filters having a collection efficiency of at least 99 percent for particles of .3 μm diameter, as measured by the DOP test, are suitable for the quantitative measurement of concentrations of suspended particulates, although some other medium, such as paper, may be desirable for some analyses. The glass-fiber filters should have a pH range of 6.5 to 7.5 (such as Gelman type A or equivalent). If a more detailed analysis is contemplated, care must be exercised to use filters that contain low background concentrations of the pollutant being investigated. Careful quality control is required to determine background values of these pollutants.

Analytical Balance - Equipped with a weighing chamber designed to handle unfolded 20.3 by 25.4 cm (8 x 10 in.) filters and having a sensitivity of 0.1 mg.

Filter Preparation - Assign number to each filter and stamp number on filter back. Expose each filter to a light source and inspect for pinholes, particles, or other imperfections. Filters with visible imperfections should not be used. Equilibrate filters in a conditioning room or desiccate for 24 hours. Silica gel or Calcium Sulfate is recommended as a desiccant. Filters should be kept between 15° to 35°C and less than 30 percent relative humidity. Weigh the filter to the nearest milligram, record tare weight, and filter identification number in record book.

Operation of Sampler (24 Hour Method) Open the shelter, loosen the wing nuts, and remove face plate from holder. Install a numbered, pre-weight, glass fiber filter in position (rough side up). Filters should not be bent or folded prior to sampling. Replace the faceplate without disturbing the filter, and fasten securely. Undertightening will allow air leakage and overtightening will damage the sponge-rubber face gasket. A filter holder using a pre-installed filter may also be used. Close the roof of the shelter after making sure no foreign objects are left under roof. Record sampling time, date, location and filter number on a flow chart and the filter envelope. Install flow chart on record (The measurement can also be done employing a rotameter in place of flow charts). Start Sampler. Check to make certain recording pen is inking properly and flow is normal. Set time to run sampler for 24 hours from midnight to midnight. As soon as practical after sampling is complete, remove recording chart. Record on the filter folder the filter number, location, sampling time and date. Also record any other factors such as meteorological conditions (wind speed, wind direction, atmospheric stability, occurrence of precipitation, insolation, ambient humidity and temperature) or nearby abnormal emission sources that might directly affect the results. If the sample is defective, void it at this time.

Anaylsis of Exposed Filter - Equilibrate the exposed filter for 24 hours in the filter conditioning environment, then reweigh to nearest milligram. After weighing, filters will be saved for detailed chemical analysis for toxic constituents. If flow charts are used, the volume of air sample can be calculated as flows: If flow varies by less than 2 cfm read chart to nearest whole number. If flow varies by more than 2 cfm read chart at least in every four hour intervals. If flow varies by more than 4 cfm read in two hour intervals. From High Volume Sampler Calibration Curve read true m^3/min. for each flow chart reading. Then add and average readings. Read total sampling time (in minutes) from flow chart, and record. Calculate total volume in m^3. If a rotameter is used, the volume of air samples can be calculated as follows: From High Volume Sampler Calibration Curve read true $m/^3$ min. from calibration curve for initial and final rotameter readings. Calculate total sampling time (in minutes) from start and stop times recorded on filter folder. Calculate total volume in m^3.

Calculate suspended particulate concentration. Keep a permanent record book including sampling location, dates, results, and related meteorological information. Analyze for toxic elements in the particulates.

II. EMISSION RATE MEASUREMENTS

Concentration Profile Technique

From early investigations of fluid flow parallel to flat interfaces it is known that a region of pure turbulent flow exists. This region is beyond the laminar sublayer immediately adjacent to the interface and beyond the buffer layer that separates the laminar sublayer from the turbulent region. In the turbulent region the velocity profile is:

$$\bar{V}_x = \frac{V_*}{K_1} \ln (y/y_o) \qquad (1)$$

where $\bar{V}_x$ is average velocity (cm/s) at height above the surface y (cm), V_* is friction velocity (cm/s), y_o is a roughness length (cm), and $K_1 = 0.4$. The concentration profile is of analogous form:

$$\bar{\rho}_{A1} = \bar{\rho}_{A1}\Big|_{\delta} - \frac{n_A}{K_1 \bar{V}_x} \ln (y/\delta) \qquad (2)$$

where $\bar{\rho}_{A1}$ is the average concentration of chemcial A (ng/L) at height y (cm), n_A is the flux rate from the surface (ng·cm/L·s), δ is a hypothetical length parameter (cm) and $\bar{\rho}_{A1}\Big|_{\delta}$ is the concentration at this length.

If the velocity and concentrations samples are from the turbulent region graphs of $\bar{V}_x$ and $\bar{\rho}_{A1}$ vs ln y will be linear. The slope of the velocity profile line, S_v, is then:

$$S_v = V_*/K_1 \qquad (3)$$

and that of the concentration profile line, S_δ, is then:

$S_p = -N_A/K_1 V_*$

The flux rate of chemical A, obtained from the two slope determination is:

$$N_A = -K_1^2 S_p S_v \qquad (5)$$

Since the turbulent diffusion is not exactly equal to turbulent kinematic viscosity $D_{A1}^{(t)}/V_1^{(t)}$ need be used as a correlation factor. In the presence of thermal turbulence another correction factor ϕm^2 is necessary. Eq. 5 modified for these corrections is:

$$N_A = -K_1^2 S_p S_v D_{A1}^{(t)}/V_1^{(t)} \phi_m^2 \qquad (6)$$

Both correction factors are a function of Richardson number, R_i (see Thibodeaux, 1979).

The concentration profile technique as outlined above has been used to measure the flux rate of pesticides from crop applications, the flux of ammonia from grazed land and the dry deposition of anthropogenic chemicals into lakes. In essence the technique has a well established theory and a history of applications.

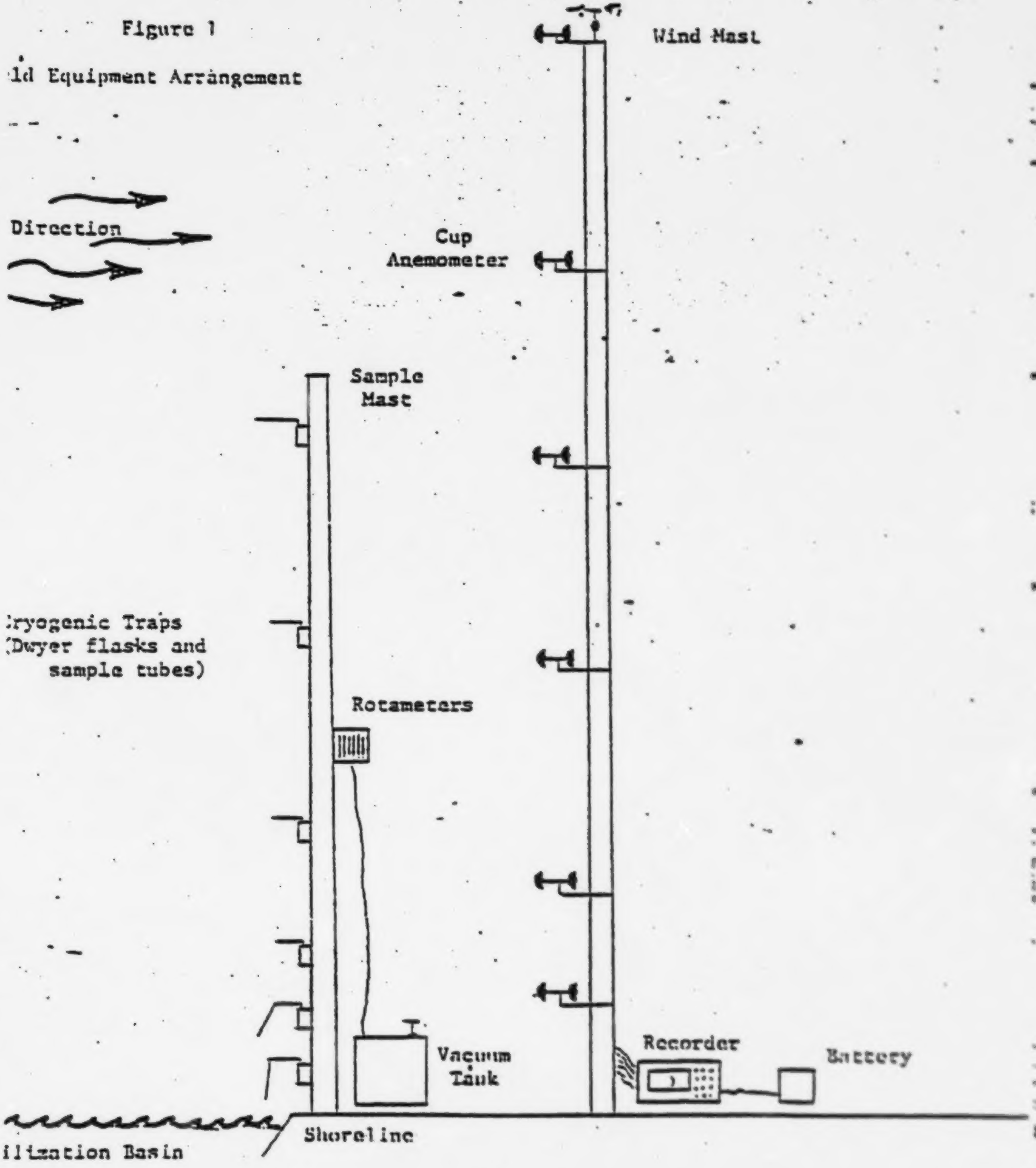
Equipment

Air Sampling Device

This device consists of a mast, 2m in height, equipped with holders at six positions for small (300 ml) Dwyar flasks and U-tube cryogenic traps (Figure 1). Tube extenders, up-stream of the traps, allow precise sample heights to be chosen and maintained. Downstream side of the U-tube traps are connected to air rotameters and

Figure 1

ld Equipment Arrangement


Wind Mast
Direction
Cup
Anemometer
Sample
Mast
ryogenic Traps
(Dwyer flasks and
sample tubes)
Rotameters
Vacuum
Tank
Recorder
Battery
Shoreline
ilization Basin

adjustable valves. Flow is maintained by a portable, hand-evacuated vacuum tank.

The sample tube, i.e., the U-tube cryogenic trap, was constructed of 1/4 inch SS tubing fitted with 30-40 mesh glass beads. Swagelok couplings were used to connect the trap to the Carle valve. (Figure 2).

Wind Velocity Profile and Direction Indicator Device

The device consists of a mast, 3.2 m in height, with cup anemometers at 20cm, 40cm, 80cm, 160 cm, 240cm, and 320 cm, and a wind direction vane mounted on top. Anemometer rotational speed and wind direction information is transmitted to appropriate recorders operated by twelve volt battery.

Wet/Dry Bulb Temperature Device

This device is a hand-held type of shielded, portable thermistor wet/dry bulb psychrometer set with digital readout. Rapid response in conjunction with a telescoping mast allows temperature profiles to be obtained very quickly with a single unit. The readout and fan are battery operated.

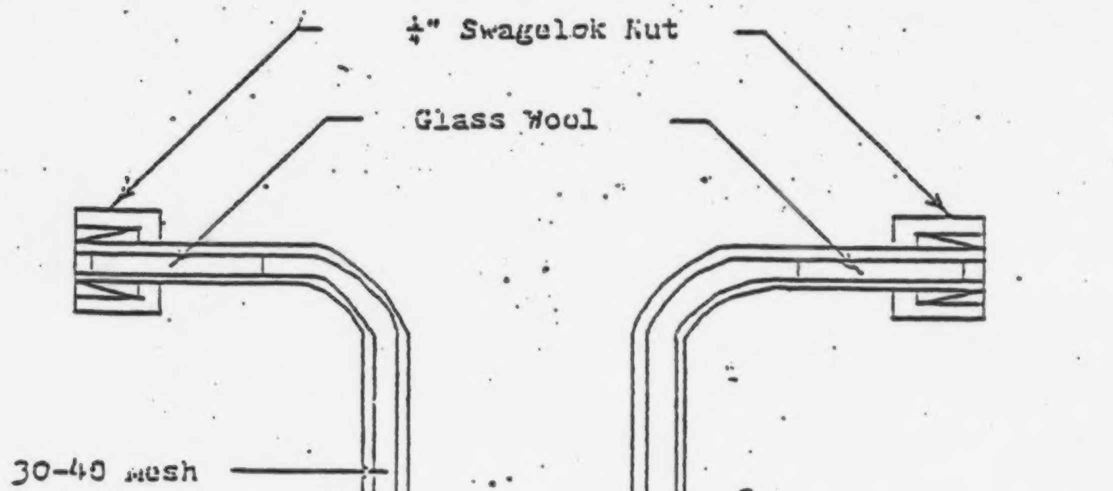
Analytical Instrumentation

The analytical instrumentation consists of a gas chromatograph (GC), an intergrator, and a recorder (Figure 3). A Perkin-Elmer Sigm 3 GC was used which is microprocessor controlled and fitted with a flame ionization detector (FIC). Through trial and error, a "waterproof" Chromosarb 102 column (6 ft. long and 1/2 inch diameter) was selected to avoid problems with the high sample humidity. Signals from the FID were integrated and recorded.

For air samples, a Carle six port, two-way valve was used to replace the lower injection port. In the first valve position, the

Figure 2

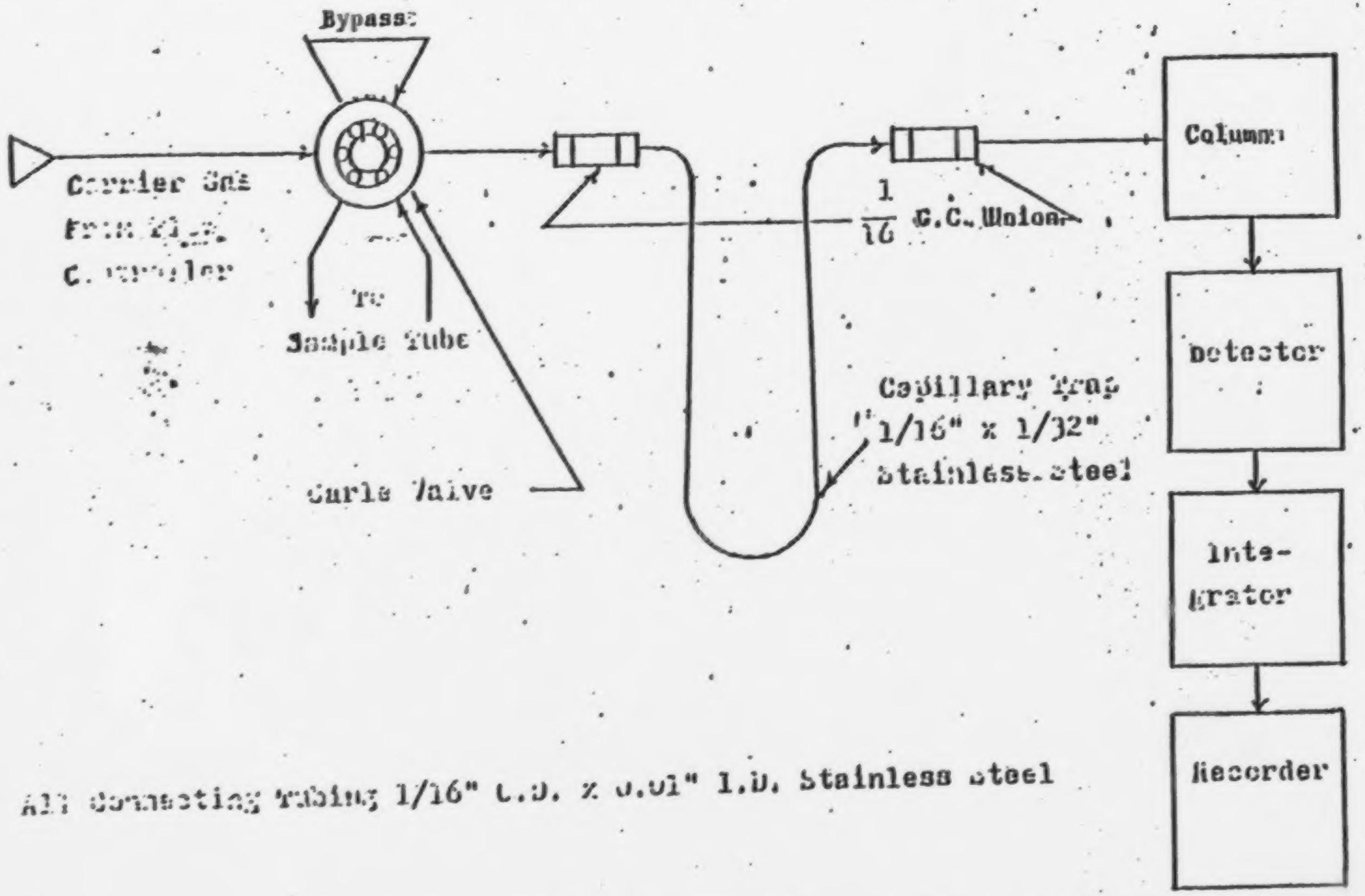
Sectional View of "U" Sample Tube


¼" Swagelok Nut
Glass Wool
30-40 Mesh Glass Beads
¼" O.D. Stainless Steel Tubing

Actual Size

Figure 3

Schematic of Gas Chromatograph


Bypass
Carrier Gas
From Flow
Controller
To
Sample Tube
Carle Valve
1/16 G.C. Union
Capillary Trap
1/16" x 1/32"
Stainless steel
Column
Detector
Integrator
Recorder

All Connecting Tubing 1/16" O.D. x 0.01" I.D. Stainless steel carrier gas flows directly through a bypass in the valve, through a capillary trap of 1/16 inch SS tubing and into the GC. In the second position, the carrier gas first sweeps out the sample from the tube, then flows through the GC.

Water samples are injected directly into the GC in one microliter aliquots.

Sampling Procedure

The sampling mast and wind mast are set up on the downwind side of the lagoon near the water surface. To ensure a good profile, the sampling location should be selected to minimize the wind interference from trees, buildings, or lagoon levees. It is desirable that the wind speed be greater than 2 mph so that a distinct profile exists.

The sampling mast is prepared by filling the Dwyar flasks with liquid oxygen. Six samples tubes are selected and placed in the Dwyar flasks. One end of each sample tube was connectaed to the tube extenders and the other to the rotameter bank (six rotameters each with a five needle valve). The exhaust of the rotameter bank is connected to the vacumm tank.

To begin sampling, the main vacuum valve is opened and each needle valve adjusted to give a flow between 100 and 250 ml/minute. A four to six minute sample is taken (0.5-1.0 liters). When the sampling period is over, all the tubes are removed, capped, and stored under liquid oxygen until they are analyzed.

Analysis Procedure

While still in liquid oxygen, the sample tubes are attached to the Carle valve, i.e., the inlet to the GC. The liquid oxygen is transferred to the capillary trap. Next, the Carle valve is turned to the sample position, a timer is started and a heat gun is directed on the sample tube simultaneously. Five hundred seconds are allowed to insure complete desorption of the sample. At the end of the desorption period, the Carle valve is turned to the bypass position and the heat gun is turned off. Next, the liquid oxygen around the capillary trap is replaced with 180°C heated bath. Simultaneously, the auto zero of gas chromotograph and the run button the integrator are pressed and the reacorders turned on. It takes 400 seconds to record the entire chromatograph. The retention times of the peaks were used to identify the organic compounds.

Methods of Calculation

Figure 4 shows the velocity and concentration profiles taken from pulp and paper mill wastewater basins. The calculation procedure is as follows: The slope of the velocity profile line in Figure 4 is S_v = 128 cm/s. The slope of the concentration profile for methanol is S_ρ = -130 ng/L. The Eq. 5 the uncorrected flux rate is:

$$N_A = -(.4)^2(-130ng/L)(128cm/s)1E\text{-}3L/cm^3$$

$$N_A = 2.66ng/cm^2 \cdot s$$

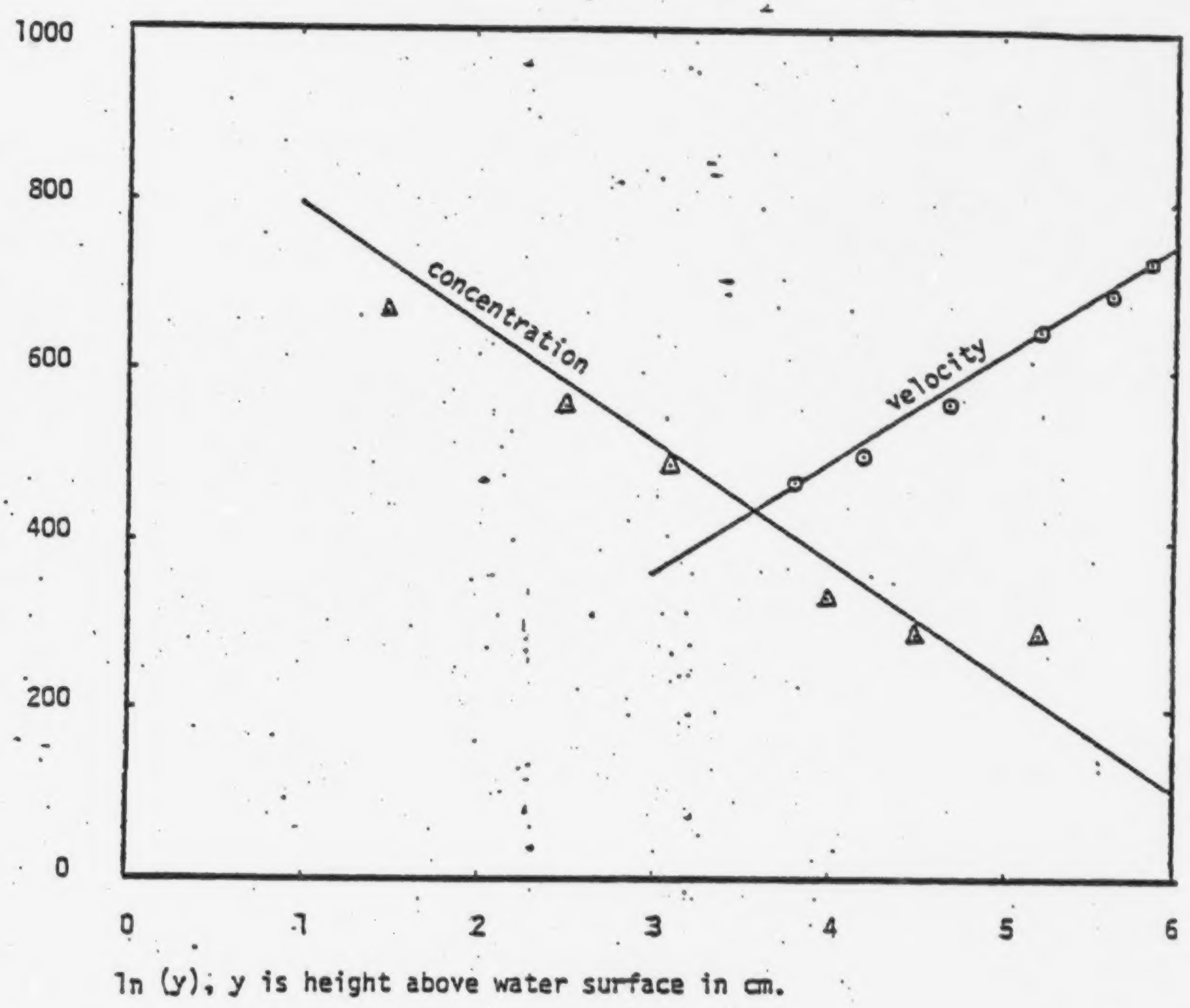
With temperature readings at the water surface and at 5 meters the Richardson number can be determined and the correction factors shown in Eq. 6 can be applied.

Advantages and Limitations of the Method

The advantages of the concentration profile technique are:

1. a well developed theory and history of application,
2. does not disturb the environment sampled,
3. amenable to cyrogenic traps and solid adsorbents,
4. simple equipment and procedure,

FIGURE 4 VELOCITY AND METHANOL CONCENTRATION PROFILES



5. self checking (i.e., data linear on semi-log graph),
6. independent of background concentrations, and
7. capable of detecting deposition.

The limitations of the concentration profile technique are:

1. need wind to use the method,
2. wind speed must be high enough to be turbulent,
3. must sample in the pure turbulent region,
4. must be well down-wind of disturbances such as high levees, trees, or buildings that distort the profiles,
5. applicable only to area emission sources, and
6. samples must be averages (i.e., several minutes) and not instantaneous values.

Part C
Control Technologies

I. Steam Stripper

In chemical, petrochemcial, and pharaceutical manufacturing industries to name a few, it is common to find many different typs of waste waters which contain various amounts of the organic pollutants. In addition, the waste water may contain conventional pollutants, and inorganic substance. The most organic pollutants are found in waste water streams as a rsult of their application as solvents or raw material, and due to their formation during the course of chemical reactions.

For example, in the manufacture of vinyl chloride by the oxychlorination and direct chlorination prcesses, 1,2-dichloroethane is formed as a result of intermediate chemical reactions and is used as raw material for cracking to vinyl chloride. the waste water generated in the process contains various amounts of several organic pollutants. These inlcude vinyl chloride, 1,2-dichloroethane, 1,1,2 -trichloroethane, and ethyl chloride. In addition, it contains other organic compounds, and inoranic salt and ions in solution. The steam stripper can be effeciently used to remove the above type of chlorinated hydrocarbons from the waste water. Incineration or recovery of the column overhead vapor is a common practice.

In other manufacturieng processes, commonly used solvents, such as benzene and toluene, are separated from an aqueous phase which may contain salt formed during reactions or neutralization. The aqueous phase waste water, in addition to being contaminated with the solvents, would contain other materials used as raw material or formed by reactions such as benzene derivatives, phenols, chloroform, etc.

The steam stripper is designed and actually used in industries to serve the purpose of removing some of the volatile organic pollutants. The steam stripped waste may be further treated in a biological treatment system, or disposed of in surface impoundments.

Steam stripping is a part of distillation processes. Nowadays the design of a distillation or steam stripping tower seldom requires pilot-plant experimentation because methods of rigorous computation by hand and computer are available for satisfactory performance design. This is accomplished through the use of technology models for stage calculations as well as for physical properties and tray efficiencies obtained from experimental correlations. The method covered in this report essentially presents the application of these technologies.

A. Thermodynamic Consideration

A large number of the organic pollutants that are sparingly soluble in water are amenable to formation of a constant-boiling heterogeneous azeotrope with water. But is should be cautioned that the organic pollutants of interest here for removal are those present as a homogeneous mixture following oil-water phase separation if necessary. This mixture form non-ideal solution with water. Removal is controlled by the vapor-liquid equilibrium compositions in dilute aqueous solutions rather than azeotropic compositions.

Vapor-liquid equilibrium relationship of the organic pollutants in a waste water forms the basis of detrmining their removability from the waste water by steam stripping. In principle, an organic pollutant can be removed from the waste water by steam striping if the vapor in equilibrium with the liquid waste water contains a higher concentration of the organic pollutant than in the water in the range of concentrations under consideration. The magnitude of the concentration difference between the waste water and its vapor serves as a measure of the removal effectiveness.

The vapor-liquids relationship between the mole fraction y_i of an organic pollutant inthe vapor and the mole fraction x_i in the mixture can be represented by thermodynamic equation:

$$y_i = \frac{\gamma_i P_i^o}{P} x_i \qquad (1)$$

where γ_i is the activity coefficient of organic pollutant i in the waste water, P_i^o is the vapor pressure at steam stripper operating temperature, and P is the total pressure. Equation (1) is a simplified form of the rigorous thermodynamic equation because at modest prssures under consideration the fugacity coefficient is close to unity and the water phase, standard stae fugacity approaches the vapor pressure at system temperature. Equation (1) can be written in terms of the vapor-liquid equilibrium constant or K-value:

$$y_i = K_i x_i \qquad (2)$$

where $K_i = \gamma_i P_i^o / P$.

A waste water stream is a multicomponent mixture containing many soluble compounds, organic or inorganic. Equation (1) or (2) is applicable as long as the activity coefficient is evaluated in a proper manner. Some experimental data would be necessary in order to use these equations.

Since most multicomponent vapor-liquid equilibrium data are often unavailable or unreliable, there are several methods of calculating the activity coefficient for multicomponent mixtures from data on the constituent binary pairs. The mathematical expressions using binary parameters serve a useful purpose of predicting multicomponent phase equilibria beyond the range covered by the experimental measurements.

Amont these are the expressions developed by Van Laar (24), Margules (23), Wilson (22), Renon (19), and more recently UNIQUAC (21) and UNIFAC (3). When the solubilities of organic pollutants in water are small, which are true to most organic compounds listed in Table 1 (except N-nitrosedimethylamine), it can be shown by the application of the mathematical expressions that the effect of a small amount of sparingly soluble organic compounds on the activity coefficient for a pair of an organic pollutant and the waste water is negligible. This is not only due to the small concentration of the other organic compounds but also due to larger deviation from ideality between the organic and water than between the organic and organic, to result in very large activity coefficients of the organic pollutants in the waste water. This phenomenon is consistent with the concept based on theories dealing with the behavior of the activity coefficient in solvent environments (6, 18, 3), because a majority portion of the solution environment in the waste water is water.

For hydrocarbon mixtures, the activity coefficient can be commonly assumed to be close to unity. If more rigor is desired, the methods such as Chao-Seader's can be used to determine the vapor-liquid equilibrium constant (27).

The effect of the presence of salt electrolytes on the activity coefficient of the dissolved organics can be considered as follows:

Table 1. Physical Properties used in the Treatability Study

I.D.	Compound	MW	BP,°C	Solubility in Water, at 20°~25°C, 10^{-3} g/L (ppm)
1.	acenaphthene	154.2	279	3.5
2.	acrolein	56.1	52.4	4x10^{5}
3.	acrylonitrile	53.1	77.3	7.3x10^{4}
4.	benzene	78.1	80.1	2.6x10^{3} at 69 °C
5.	benzidine	184.2	400	4x10^{2}
6.	carbon tetrachloride (tetrachloromethane)	153.8	76.8	8x10^{2}
7.	chlorobenzene	112.6	132.0	4.9x10^{2}
8.	1,2,4-trichlorobenzene	181.5	213	550*
9.	hexachlorobenzene	284.8	309	50
10.	1,2-dichloroethane	99.0	83.5	8.7x10^{3}
11.	1,1,1-trichloroethane	133.4	133.8	4.4x10^{3}
12.	hexachloroethane	236.7	186.9	50
13.	1,1-dichloroethane	99.0	57.3	5.5x10^{3}
14.	1,1,2-trichloroethane	133.4	133.8	4.5x10^{3}
15.	1,1,2,2-tetrachloroethane	167.9	146.2	2.9x10^{3}
16.	chloroethane	64.5	12.3	5.74x10^{3}
17.	bis(chloromethyl) ether	114.9	104	Decompose
18.	bis(2-chloroethyl) ether	143.0	178.5	10.2x10^{3}
19.	2-chloroethyl vinyl ether (mixed)	106.6	108	1.5x10^{4}
20.	2-chloronaphthalene	162.6	256	7.9
21.	2,4,6-trichlorophenol	197.5	246	9x10^{2}
22.	parachlorometa cresol	142.6	235	4x10^{3}
23.	chloroform (trichloromethane)	119.2	61.2	8.2x10^{3}
24.	2-chlorophenol	128.6	176	2.85x10^{4}
25.	1,2-dichlorobenzene	147	180.4	1.45x10^{2}
26.	1,3-dichlorobenzene	147	172	1.23x10^{2}
27.	1,4-dichlorobenzene	147	174.4	7.9x10^{2}
28.	3,3-dichlorobenzidine	253.1		6x10^{3}*
29.	1,1-dichloroethylene	96.9	37	4x10^{2}
30.	1,2-trans-dichloroethylene	96.9	48.1	6x10^{2}
31.	2,4-dichlorophenol	163	210	4.5x10^{3}
32.	1,2-dichloropropane	113	96.8	2.7x10^{3}
33.	1,3-dichloropropylene (1,3-dichloropropene)	111	108	1.7x10^{3}*
34.	2,4-dimethylphenol	122.2	211.5	4.7x10^{3}*
35.	2,4-dinitrotoluene	182.1	300	270

*predicted from the partition coefficient.

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36.	2,6-dinitrotoluene	182.1		300^{*}
37.	1,2-diphenylhydrazine	184.2		588^{*}
38.	ethylbenzene	106.2	136.2	1×10^{2}
39.	fluoranthene	202.3	250 at 8 kPa	0.25
40.	4-chlorophenyl phenyl ether	205.7		$1.48\times10^{5*}$
41.	4-bromophenyl phenyl ether	249.1	310.1	$1.44\times10^{5*}$
42.	bis(2-chloroisopropyl) ether	171	189	1.7×10^{3}
43.	bis(2-chloroethoxy) methane	177	106	8%
44.	methylene chloride (dichloromethane)	84.9	40.2	2×10^{4}
45.	methyl chloride (chloromethane)	50.5	-24	7.25×10^{3}
46.	methyl bromide (bromomethane)	94.9	3.5	9×10^{2}
47.	bromoform (tribromomethane)	252.8	149.6	2.89×10^{3}
48.	dichlorobromomethane	163.8	90	
49.	trichlorofluoromethane	137.4	24.8	1.1×10^{3}
50.	dichlorodifluoromethane	120.9	-29.8	28
51.	chlorodibromomethane	208.3	120	
52.	hexachlorobutadiene	260.8	215	2
53.	hexachlorocyclopentadiene	273	239	12.6^{*}
54.	isophorone	138.2	215.2	$9.6\times10^{3*}$
55.	naphthalene	128.2	218	30
56.	nitrobenzene	123.1	210.9	1.9×10^{3}
57.	2-nitrophenol	139.1	217.2	2.1×10^{3}
58.	4-nitrophenol	139.1	279	1.6×10^{4}
59.	2,4-dinitrophenol	184.1		$5.\times10^{3}$
60.	4,6-dinitro-o-cresol	198.1		$1.5\times10^{4*}$
61.	N-nitrosodimethylamine	74.1	153	infinite
62.	N-nitrosodiphenylamine	198.1		$2\times10^{3*}$
63.	N-nitrosodi-n-propylamine	130.2	205.9	7.6
64.	pentachlorophenol	266.4	310	14
65.	phenol	94.1	181.8	8.66×10^{4}
66.	bis(2-ethylhexyl) phthalate	391	386.9 at 0.67 KPa	50
67.	butyl benzyl phthalate	312	377	0.0036^{*}
68.	di-n-butyl phthalate	278.3	340	4.5×10^{3}
69.	di-n-octyl phthalate	390		0.006^{*}
70.	diethyl phthalate	222.2	298	1×10^{3} at 32°C
71.	dimethyl phthalate	194.2	282	4×10^{3}
72.	1,2-benzanthracene	228.3	435	0.011
73.	benzo (a) pyrene (3,4-benzopyrene)	252.3	31 at 1.33 kPa	1.2×10^{-3}
74.	3,4-benzofluoranthene	250.3		1.2×10^{-3}
75.	11,12-benzofluoranthene	250.3	480	1.2×10^{-3}
76.	chrysene	228.3	448	0.002 ~ 0.006
77.	acenaphthylene	152.2	270	3.93
78.	anthracene	178.2	340	0.073
79.	1,12-benzoperylene	276.3		2.6×10^{-4}
80.	fluorene	152.2	294	1.98
81.	phenanthrene	178.2	340	1.29

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6.3.2 Quantitation

The quantitation of constituents in ambient air samples is accomplished either by utilizing the total ion current monitor, or where necessary, from extracted ion current profiles. In order to eliminate the need to obtain complete calibration curves for each compound for which quantitative information is desired, the method of relative molar response (RMR) factors is used. Successful use of this method requires information on the exact amount of standard added and the relationship of RMR (unknown) to the RMR (standards).

6.3.2.1 RMR Determination

The compounds to be quantified are loaded onto Tenax GC cartridges using a permeation system or in cases where permeation tubes are not available the vaporization system shown in Figure 4 is used.

With the vaporization method helium is purified by passing it through a cryogenic trap followed by two carbon traps. The standards and substances to be quantified are prepared in methanol and 2.0 µℓ solution is injected through the septum of the heated loading tube (250°C). The vaporized components are swept onto the Tenax GC cartridge at a rate of 200 ml/min for 6 min (total He 1.2 ℓ). Because of the low breakthrough volume for methanol (0.8 ℓ at 70°F), the majority is passed from the cartridge. This system is used to load relatively non-volatile compounds with breakthough volumes >30 ℓ.

The method of calculating RMRs is as follows:

$$(1)\quad \text{RMR}_{\text{unknown/standard}} = \frac{A_{unk}/\text{Moles}_{unk}}{A_{std}/\text{Moles}_{std}}$$

A = system response, height or area determined by integration or triangulation.

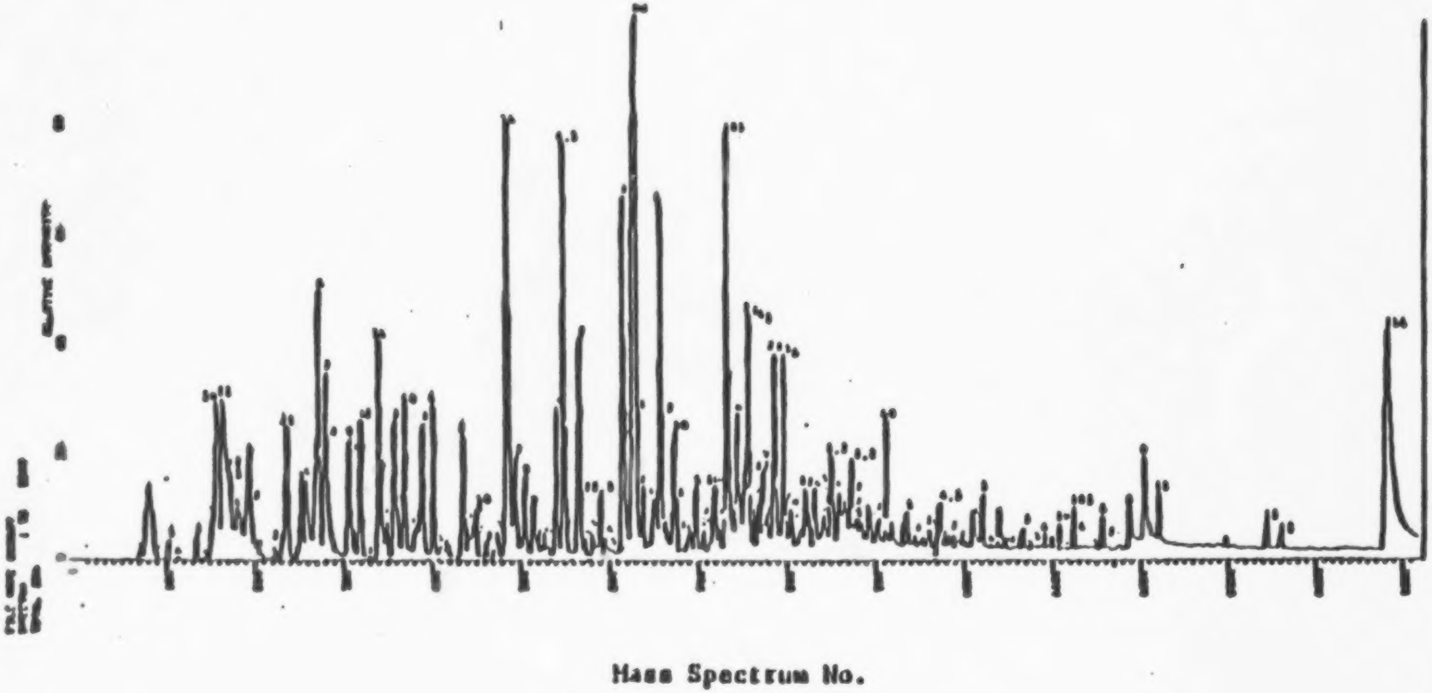

Figure 2. Profile of ambient air pollutants obtained using high resolution gas chromatography/mass spectrometry/computer.

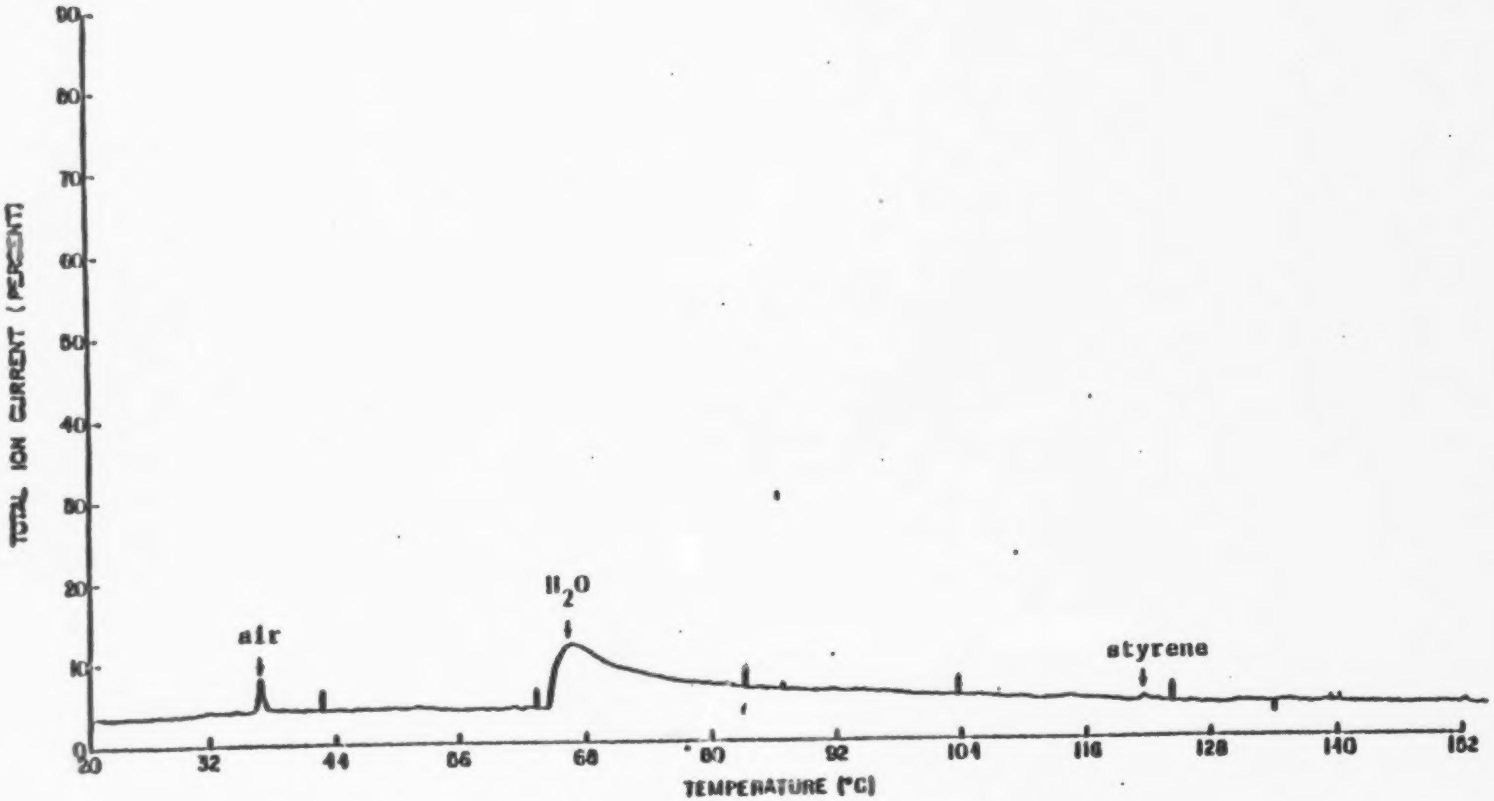

Figure 3. Background profile for Tenax GC cartridge blank.

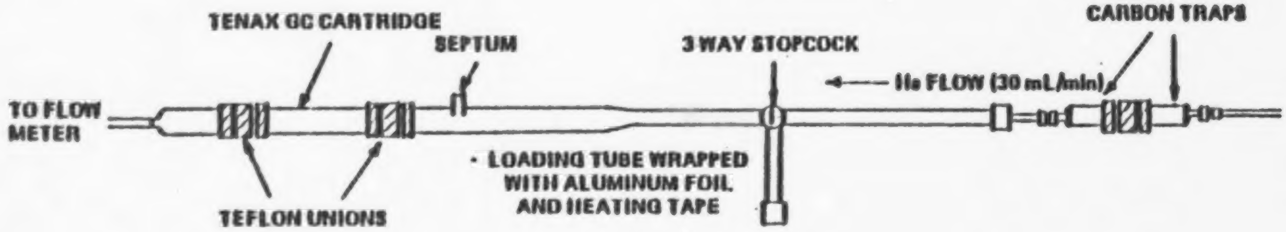
TENAX GC CARTRIDGE
SEPTUM
3 WAY STOPCOCK
CARBON TRAPS
He FLOW (30 mL/min)
TO FLOW METER
TEFLON UNIONS
LOADING TUBE WRAPPED WITH ALUMINUM FOIL AND HEATING TAPE

Figure 4. Schematic of vaporization unit for loading organics dissolved in methanol onto Tenax GC cartridges.

unk = unknown

std = standard

The value of RMR is determined from at least three independent analysis of samples. Linearity over the dynamic range and an intercept of zero has been previously described.

$$(2)\ RMR_{unk/std} = \frac{A_{unk}/g_{unk}/GMW_{unk}}{A_{std}/g_{std}/GMW_{std}}$$

A = system response, as above

g = number of grams present

GMW = gram molecular weight

$$(3)\ g_{unk} = \frac{A_{unk} \cdot GMW_{unk} \cdot g_{std}}{A_{std} \cdot GMW_{std} \cdot RMR_{unk/std}}$$

6.3.2.2 Calculation of Ambient Air Concentrations

Since the volume of air taken to produce a given sample is accurately known and an external standard is added to the sample, then the weight per cartridge and hence the concentration of the unknown pollutants in this study requires that the RMR be determined for each constituent of interest during the analysis of field samples. Every sixth cartridge is a control cartridge for determining

RMRs for each compound (calibration of instrument, storage and recovery). This means that when an ambient air sample is taken, the external standard is added at a known concentration prior to analysis. It is not imperative at this point to know what the RMR of each of the constituents in the sample happens to be. However, after the unknowns are identified then the RMR can subsequently be determined and the unknown concentration calculated in the original sample using the RMR. In this manner it is possible to obtain qualitative and quantitative information on the same sample with a minimum of effort.

Once the quantity of substance per cartridge has been determined, the level in the ambient air is given by

$$\frac{ug}{m^3} = \frac{ug_{unk} \cdot 1000\ L}{m^3 \cdot \text{Volume Sampled (L)}}$$

7.0 Quality Assurance Program

7.1 Reagent and Glassware Control

Reagent and glassware control is required in order to minimize contamination. Sample containers, glassware, etc. are cleaned with Isoclean®, rinsed with distilled/deionized water and heat treated at 450-500°C to insure the removal of all traces of organic compounds.

7.2 Sampling Protocol and Chain of Custody

As part of the quality control procedures, sampling protocols and chain of custody forms are prepared for each sampling cartridge. The fate of each sampling cartridge is tracked from the time they are prepared until the data has been reduced to a finished form.

7.3 Blanks, Controls, Standards, and System Performance Samples

7.3.1 Blanks

Ten percent of the sampling cartridges from each batch are set aside to serve as blanks to be analyzed for background contamination. After the preparation of a set of sampling cartridges, one cartridge is checked for background prior to their committment to field sampling. Blank (unused) cartridges travel to the field site returned to the laboratory and stored along with the field samples at -20°C until ready for analysis.

7.3.2 Controls

Ten percent of the sampling cartridges are loaded with the deuterated compounds listed in 6.2.1. Sampling with control cartridges allow for an assessment of premature breakthrough if it occurs. Control cartridges are analyzed along with other samples and since deuterated compounds are employed the qualitative and quantitative analysis of these samples proceeds unimpeded.

7.3.3 Standards for RMR Determination

The compounds listed in Table 1 are loaded onto Tenax GC cartridges from a permeation system. A minimum of three analyses is required for determining RMRs for a set of samples which are quantitatively analyzed.

7.3.4 System Performance Mixtures

The system performance standards listed in Table 7 are loaded onto Tenax GC cartridges (using the vaporization method) to determine mass calibration and intensity and chromatograhic performance of the GC/MS/COMP system.

Table 7. GC/MS/COMP SYSTEM PERFORMANCE STANDARDS

Compound	Quantity (ng)
Perfluorokerosene	350
Perfluorotoluene	350
Ethylbenzene	300
p-Xylene	300
n-Octane	300
n-Decane	300
1-Octanal	300
5-Nonanone	300
Acetophenone	300
2,6-Dimethylaniline	300
2,6-Dimethylphenol	300

7.4 Sample Analysis

To insure the accuracy and precision of the data acquired instrument and chromatographic performance are monitored on a daily basis.

7.4.1 Instrument Calibration

Calibration of mass and intensity of magnetic systems employ perfluorokerosene. Table 8 lists the tolerances for each mass and intensity which the mass spectrometer must achieve.

Perfluorotoluene in the performance mixture is employed for determining instrument stability as related by mass resolution and relative ion abundance under GC condtions. The masses and intensities listed in Table 8 are compared to the results obtained on a daily basis and for each set of samples analyzed.

7.4.2 Assessment of Chromatographic Performance

The quality of the chromatography is of utmost importance since the accuracy and precision of qualitative and quantitiative analysis are directly affected. Glass capillary columns are evaluated according to the following criteria:

(1) percent peak asymmetry factor (PAF)

$$\% \text{ PAF} = \frac{B}{F} \times 100$$

where B = the area of the back half of a chromatographic peak

F = area of the front half of the chromatographic peak both measured 10% above baseline

(2) effective Height Equivalent to a Theoretical Plate ($HETP_{eff}$)

$$HETP_{eff} = \frac{L}{5.54\ (X/Y)^2}$$

Table 8. MASS AND INTENSITY TOLERANCES ACCEPTABLE FOR CALIBRATION OF MAGNETIC INSTRUMENTS FOR QUANTITATION

Perfluorotoluene[a]		Perfluorokerosene	
m/z	%I (C.V.)	*m/z*	%I (C.V.)
69	33 (5)	51	39 (10)
79	11 (10)	100	22 (8)
93	16 (8)	119	100 (0)
117	43 (8)	131	89 (5)
167	15 (7)	169	58 (4)
186	59 (5)	181	62 (6)
217	100 (0)	219	24 (5)
236	66 (4)	231	29 (8)

[a] To be achieved in the chromatography mode.

where X = the corrected retention distance for sweep time of the compound,

Y = chromatographic peak and width at 1/2 height,

L = column length (mm)

(3) separation number (SN)

$$SN = \frac{D}{W_1 + W_2} - 1$$

where D = the distance between two peaks,

W_1, W_2 = widths at 1/2 height

(4) resolution (R)

$$R = \frac{2 \quad \Delta W}{W_1 + W_2}$$

where ΔW = average base width,
W = peak width at base

(5) Acidity and Basicity

$$\text{Acidity} = \frac{\text{weak base (peak area or height)}}{\text{acetophenone (peak area or height)}}$$

$$\text{Basicity} = \frac{\text{weak acid (peak area or height)}}{\text{acetophenone (peak area or height)}}$$

The use of the compounds listed in Table 7 provides information as to the degree of adsorption and the type of adsorption mechanisms. 1-Octanol and 5-nonanone serves to determine the extent of deactivation of the glass surface (PAF). The acidity and basicity of the glass capillary column are assessed by the adsorption of weak bases and acids, respectively.

The resolution and separation number are determined for the compound pairs ethylbenzene: p-xylene and octane:decane, respectively. $HETP_{eff}$ is based on octane. Table 9 lists the minimum performance specifications acceptable for ambient air analysis.

Table 9. SPECIFICATIONS OF PERFORMANCE FOR GLASS CAPILLARY COLUMN[a]

Parameter	Test Compound(s)	Value ± S.D. (C.V.)
Resolution	Ethylbenzene:p-Xylene	1.30 ± 11
Separation No.	Octane:Decane	73 ± 6
% Peak Asymmetry Factor	1-Octanol	239 ± 141
	Nonanone	130 ± 32
	Acetophenone	260 ± 34
Acidity	2,6-Dimethylaniline:Acetophenone	1.00 ± 0.07
Basicity	2,6-Dimethylphenol:Acetophenone	0.82 ± 0.03

[a] SE-30 WCOT/$BaCO_3$, 0.48 mm i.d. x 75 m, 1 μ film thickness.

7.4.3 Sequence of Sample Analysis

A strict step-sequence of analysis is followed. Upon mass and intensity calibration of the MS system, a Tenax GC cartridge loaded with the performance mixture is first analyzed. Following the performance mixture a blank and an RMR standard mixture is analyzed next, then five samples. The cycle begins with the performance mixture, bland and RMR standards. Thus, 30% of the cartridges analyzed consist of control samples.

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82.	1,2,5,6-dibenzanthracene	278.4		$5x10^{-4}$
83.	indeno (1,2,3-C,D) pyrene	276.3		$1.3x10^{-3}$
84.	pyrene	202	360	$8.2x10^{-3}$
85.	tetrachloroethylene	165.8	121	$1.5x10^{2}$
86.	toluene	92.1	110.6	$5.35x10^{2}$
87.	trichloroethylene	131.4	87	$1.1x10^{3}$
88.	vinyl chloride (chloroethylene)	62.5	-13.4	$2.5x10^{3}$ at 1 atm P.P.
89.	PCB-1242 (AROCHLOR 1242)	266.5	346	0.24
90.	PCB-1254 (AROCHLOR 1254)	328.4	368	$1.2x10^{-2}$
91.	PCB-1221 (AROCHLOR 1221)	200.7	298	15
92.	PCB-1232 (AROCHLOR 1232)	232.2	308	1.45
93.	PCB-1248 (AROCHLOR 1248)	299.5	358	$5.4x10^{-2}$
94.	PCB-1260 (AROCHLOR 1260)	377.5	408	$2.7x10^{-3}$
95.	PCB-1016 (AROCHLOR 1016)	257.9	341	0.34
96.	BHC-Alpha	290.83		$4.4x10^{4}$ at 15°C
97.	BHC-Beta	290.83		$1.3x10^{3}$
98.	BHC-Gamma	290.82		
99.	BHC-Delta	290.83		

Since the addition of the electrolytes will lower the vapor pressure of water, the activity coefficient of water (vapor pressure of water at various salt concentrations/[pure water vapor pressure x water mole fraction]) will decrease as the salt concentration is increased. In principle, once the vapor pressure lowering effect is known, the activity coefficient of the organic material can be calculated by use of the Gibbs-Duhem relation. The examination of the Gibbs-Duhem relation reveals that the activity coefficient of the organic material when the salt concentration is zero. As the salt concentration is increased, the activity coefficient of the organic material increases, representing the "salting-out" effects. The separation of the organic matter by stream stripping will be enhanced in the presence of salts in solution. The use of activity coefficients corresponding to the zero concentration represents the minimum separation possible as far as the effect of electrolytic salts is concerned.

The experimental vapor-liquid data should be used to calculate the activity coefficients of the organic pollutants in water. When these data are not available, the activity coeficients are calculated from liquid-liquid mutual solubility data, and from the correlation developed for aromatic solutes in dilute aqueous solutions based on solid-liquid equilibrium data (7). In cases where neither of the above information could be found, the activity coefficients could be determined using the partition coefficient data, and the method of UNIFAC (3).

If organic pollutants form two partially miscible liquid phases, when mixed with water, this behavior is the indicationof the deviations of the activity coefficients from unity due to the increase in the chemical dissimilarity between the components (the organic pollutants and the waste water in this case). When the water-rich phase containing x_2 mole fraction of an organic priority pollutant comes in equilibrium with the organic rich phase, the equilibrium can be represented by:

$$x_2 \gamma_2 = x_2' \gamma_2 \qquad (3)$$

where γ_2 is the activity coefficient of the organic pollutant (component 2) in the water phase, and γ_2' and x_2' are the activity coefficient and mole fraction of the organic in the organic phase. The mole fractions x_2 and x_2' are called the mutual solubilities, and the ratio x_2'/x_2 is called the partition (or distribution) coefficient.

If the solubility of water in the organic pollutant compound is small, Equation (3) can be conveniently simplified to

$$\gamma_2 = \frac{1}{x_2} \qquad (4)$$

The activity coefficient based on the solubility data is calculated using Equation (4).

For systems in which the solubility of water in the organic pollutant compound is substantial, the activity coefficient can be determined by means of the van Larr equation

$$\ln \gamma_2 = \frac{B}{\left(1 + \frac{B}{A} \frac{x_2}{x_1}\right)^2} \qquad (5)$$

The relationship needed to determine the constants A & B using the mutual solubility data is given by Carlson and Colburn (25). For solid-liquid equilibria, the activity coefficient can be determined from the measurements using the relationship $\gamma_2 = x \text{ ideal}/x_2$, where the ideal solubility, x ideal, is a function of temperature and heat of fusion.

The correlation of the activity coefficients of aromatic organic compounds in dilute aqueous solutions given by Tsonopoulos and Prausnitz (7) is convenient to use. For the mixtures forming solid-liquid equilibria, the basis of the empirical correlation is explained in the reference.

For the mixtures of water and the organic pollutants belonging to the condensed polycylic hydrocarbons (naphthalene, anthracene, etc.) which exist as the solid state at room temperature the activity coefficients are calculated from

$$\log \gamma_2 \text{ dil} = 3.3950 + 0.35794 \; (nc - 6) \qquad (6)$$

where γ_2 dil is the activity coefficient at nearly infinite dilution, and nc is the total number of carbon atoms in the organic pollutant.

For the mixtures of water and the organic pollutants belonging to the group of the monocyclic hydrocarbons with straight saturated side chain, where no liquid solubility data are available, the activity coefficients are calculated from

$$\log \gamma_2 \text{ dil} = 3.3918 + 0.58259 \; (nc - 6) \qquad (7)$$

The methodologies representd by the above two semi-empirical correlations are essentially the extension of the analysis described by Pierotti and Deal (9).

The correction factors applicable to the logarithm of the activity coefficients are useful and reported or the organic pollutant of the ring substituted type. It is stated in the literature (7) that the temeperature dependence of the activity coefficient of aromatic compounds in dilute aqueous solutions is not well established due to insufficient data, and the variation in the activity coefficient appears to be small in the temperature range investigated (0 to 30°C).

The temperature dependence of the activity coefficient at constant composition can be represented by

$$\left(\frac{\ln \gamma_2}{T} \right)_p = - \left(\frac{\bar{H}_1 - H_1^o}{R\, T^2} \right) \qquad (8)$$

where the quantity $\bar{H}_1 - H_1^o$ is the diferential heat of solution at the temperature of the solution. Equation (8) is conveniently integrated at the constant differential heat of solution at the temperature of the solution to obtain.

$$T_1 \, (\ln \ \gamma_2)_{T_1} = T_2 \, (\ln \ \gamma_2)_{T_2} \qquad (9)$$

This approximate relation permits obtaining γ_2 at a different temperature under consideration from γ_2 at a known temperature over a narrow temperature range.

As a last resort where no experimental data are available, the activity coefficient can be computed from the UNIFAC model based on the group-contribution concept (3).

Since the activity coefficient is dependent upon the concentration of the organic pollutants in water, it is important to examine the magnitude of its variation. As removal of the volatile organic pollutant occurs in the steam stripper, its concentration will decrease in the waste water, ultimately reaching the state of infinite dilution. It is easy to extrapolate the activity coefficients at its saturation to infinite dilution in the water, as it can be determined using the two-suffix Margules equation

$$\ln \gamma_2^{\infty} = \frac{\ln \gamma_2}{(1 - x_2)^2} \qquad (10)$$

The experimental vapor pressure data can be plotted on the Cox chart to facilitate their interpolation to desired temperatures. For the vapor pressures of the organic pollutants for which the experimental data are lacking, the Clapeyron equation coupled with boiling points and Trouton's rules can be employed for estimation.

The task of constructing a basis for the vapor-liquid equilibria is necessary to organize the use of the experimental vapor-liquid equilibrium data, data on solid-liquid and liquid-liquid equilibria, and other useful correlations and methods mentioned above. Since the system of special interest is mostly the dilute region vapor-liquid equilibria of the organic pollutants in the waste water, the utility of the activity cofficients at saturation and nearly infinite dilution in virtually water solvent environment is of considerable value in carrying our quantitative analysis of otherwise complicated solution systems.

Table 2 summarizes the values of the activity coefficient, vapor pressures, and vapor-liquid equilibrium constants, for selected organic pollutants.

In Column II, the range of the activity coefficients is indicated if its variation is noticeable between saturation concentration and infinite dilution. Since the stripper operating conditions are chosen at 1 atmosphere and near 100°C, the temperature corection is applied using Equation (9) if the solubility data or the applicablility of the correlations is reported at temperatures below 100°C. Perhaps this approach may, in some cases, give lower activty coefficients in view of the finding that the variation in the infinte dilution activity coefficients is small in the range 0 to 30°C. But s is conservative.

Table 2. Summary of Thermodynamic Properties and Vapor-Liquid Equilibrium Constants

I.D.	Compound	Range of Activity Coefficients	Method of Evaluation for Activity Coeff.	Vapor Press at 100°C(kPa)	Average K values
1.	acenaphthane	63,000	Reference 7	0.61	381
2.	acrolein	17 --5.9	Reference 1	400	45.2
3.	acrylonitrile	17.5 - 14.3	Reference 1	196	30.75
4.	benzene	654.2 - 665.7	Reference 2	187	1215
5.	benzidine	290	Reference 7	0.02	0.06
6.	carbon tetrachloride (tetrachloromethane)	1654	Solubility data	200	3264
7.	chlorobenzene	1907	Solubility data	38.7	727.7
8.	1,2,4-trichlorobenzene	24553	Reference 7	3.3	795
9.	hexachlorobenzene	3,775,000	Reference 7	0.06	2285
10.	1,2-dichloroethane	173	Solubility data	167	284
11.	1,1,1-trichloroethane	378	Solubility data	213	796
12.	hexachloroethane	21387	Solubility data	4.8	1013
13.	1,1-dichloroethane	249	Solubility data	333	819
14.	1,1,2-trichloroethane	371	Solubility data	66	240.7
15.	1,1,2,2-tetrachloroethane	634	Solubility data	25	154.3
16.	chloroethane	110.7	Reference 2	1173	1282
17.	bis(chloromethyl) ether	decomposes in water.			
18.	bis(2-chloroethyl) ether	204	Solubility data	7.6	15.3
19.	2-chloroethyl vinyl ether (mixed)	119	Solubility data	81	95.5
20.	2-chloronaphthalene	61,100	Reference 7	0.73	442
21.	2,4,6-trichlorophenol	1933	Reference 7	0.5	9.4
22.	parachlorometa cresol	376	Reference 7	2.2	8.2
23.	chloroform (trichloromethane)	210	Solubility data	307	635.5
24.	2-chlorophenol	77	Solubility data	10.7	8.1
25.	1,2-dichlorobenzene	5392	Solubility data	8.1	429.2
26.	1,3-dichlorobenzene	7121	Solubility data	10.8	758.9
27.	1,4-dichlorobenzene	14,200	Reference 7	9.7	1364
28.	3,3-dichlorobenzidine	65	Reference 7	0.021	0.013
29.	1,1-dichloroethylene	1990	Solubility data	720	14139
30.	1,2-trans-dichloroethylene	1439	Solubility data	493	7005
31.	2,4-dichlorophenol	479	Reference 7	1.9	8.8
32.	1,2-dichloropropane	489	Solubility data	111	535.3
33.	1,3-dichloropropylene (1,3-dichloropropene)	694.6	UNIFAC	81	557.5
34.	2,4-dimethylphenol	257	Reference 7	2.0	5.2
35.	2,4-dinitrotoluene	5028	Reference 7	0.36	17.9
36.	2,6-dinitrotoluene	5028	Reference 7	0.36	17.9
37.	1,2-diphenylhydrazine	19	Partition Coeff.	0.03	0.006
38.	ethylbenzene	2730	Reference 2	33.9	912.4

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39.	fluoranthene	1,000,000	Reference 7	0.15	0.14
40.	4-chlorophenyl phenyl ether	2948	Reference 7	0.13	3.9
41.	4-bromophenyl phenyl ether	4418	Reference 7	0.23	9.9
42.	bis(2-chlornisopropyl) ether	985	Solubility data	6.0	58.3
43.	bis(2-chloroethoxy) methane	44	Solubility data	1.8	0.78
44.	methylene chloride (dichloromethane)	227 - 159	Reference 1	600	941.4
45.	methyl chloride (chloromethane)	37.2	Reference 2	4026	1478
46.	methyl bromide (bromomethane)	1023	Solubility data	1840	18575
47.	bromoform (tribromomethane)	881	Solubility data	21.9	190
48	dichlorobromomethane	197	Comparison of group Contribution	135	262
49.	trichlorofluoromethane	1172	Solubility data	840	9715
50.	dichlorodifluoromethane	19871	Solubility data	3266	640578
51.	chlorodibromomethane	416	Solubility data	57	235
52.	hexachlorobutadiene	5680	UNIFAC	2.7	149.5
53.	hexachlorocyclopentadiene	72,114	UNIFAC	0.72	512.4
54.	isophorone	207.6	UNIFAC	2.5	5.2
55.	naphthalene	15,127	Reference 7	2.5	368
56.	nitrobenzene	621	Solubility data	2.7	16.6
57.	2-nitrophenol	632	Solubility data	2.1	12.9
58.	4-nitrophenol	53	Reference 7	0.65	0.34
59.	2,4-dinitrophenol	97	Reference 7	<0.65	<0.63
60.	4,6-dinitro-o-cresol	308	Reference 7	<0.65	<2.0
61.	N-nitrosodimethylamine	1.12 - 3.6	Partition Coeff.	22.7	0.8
62.	N-nitrosodiphenylamine	990	Partition Coeff.	0.02	0.2
63.	N-nitrosodi-n-propylamine	59,700	Solubility data	2.9	1728
64.	pentachlorophenol	31,500	Reference 7	0.03	10.4
65.	phenol	43	Reference 1	5.3	2.26
66.	bis(2-ethylhexyl) phthalate	31,900	Solubility data	0.0002	0.063
67.	butyl benzyl phthalat	54,000,000	Partition Coeff.	0.04	21316
68.	di-n-butyl phthalate	668	Solubility data	0.009	0.06
69.	di-n-octyl phthalate	54,000,000	Partition Coeff.	0.02	9947
70.	diethyl phthalate	2216	Solubility data	0.08	1.78
71.	dimethyl phthalate	639	Solubility data	0.08	0.513
72.	1,2-benzanthracene	4,560,000	Reference 7	0.008	348
73.	benzo (a) pyrene (3,4-benzopyrene)	19,025,000	Reference 7	0.0035	650
74.	3,4-benzofluoranthene	9,320,000	Reference 7	0.0023	208
75.	11,12-benzofluoranthene	9,320,000	Reference 7	0.0023	208
76.	chrysene	2,236,000	Reference 7	0.0053	118
77.	acenaphthylene	63,000	Reference 7	9.3	5,800
78.	anthracene	282,770	Reference 7	0.006	15.0
79.	1,12-benzoperylene	78,300,000	Reference 7	1.3×10^{-7}	0.104
80.	fluorene	128,700	Reference 7	0.17	220

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81.	phenanthrene	262,800	Reference 7	0.05	138
82.	1,2,5,6-dibenzanthracene	79,300,000	Reference 7	9.3	7,300,000
83.	indeno (1,2,3-C,D) pyrene	79,300,000	Reference 7	9.3	7,304,000
84.	pyrene	1,095,000	Reference 7	0.035	375
85.	tetrachloroethylene	6690	Solubility data	53.3	3,521
86.	toluene	1569	Reference 2	74.7	1,156
87.	trichloroethylene	1131	Solubility data	150	1,674
88.	vinyl chloride (chloroethylene)	145	Reference 4	3240	4,627
89.	PCB-1242 (AROCHLOR 1242)	1,028,000	Reference 7	0.1	1,000
90.	PCB-1254 (AROCHLOR 1254)	1,028,000	Reference 7	0.05	528
91.	PCB-1221 (AROCHLOR 1221)	1,028,000	Reference 7	0.39	3,922
92.	PCB-1232 (AROCHLOR 1232)	1,028,000	Reference 7	0.29	2,908
93.	PCB-1248 (AROCHLOR 1248)	1,028,000	Reference 7	0.07	703
94.	PCB-1260 (AROCHLOR 1260)	1,028,000	Reference 7	0.02	196
95.	PCB-1016 (AROCHLOR 1016)	1,028,000	Reference 7	0.11	1,150
96.	BHC-Alpha	3,775,000	Reference 7	0.11	3,974
97.	BHC-Beta	3,775,000	Reference 7	0.61	22,849
98.	BHC-Gamma	3,775,000	Reference 7	0.17	6,547
99.	BHC-Delta	3,775,000	Reference 7	0.23	8,444

In Column III, information on the references or methods used in determining the activity coefficients is given. Column IV lists the vapor pressures of the pure organic pollutants at 100°C. Column V is the product of Column II and Column IV in accordance with Equation (2).

B. Steam Stripping Columns

Steam stripping in this application is a mass-transfer operation in which a waste water stream is contacted with live steam to remove one or more of the soluble or sparingly soluble organic pollutant components of the waste water stream by driving them into the vapor. Steam stripping is different from distrillation in that the liquid and vapor phases usually do not contain all of the same components. However, the apparatus used in the distillation application is also used for steam stripping. The equipment used for steam stripping includes perforated trays and packed towers.

1. Stage Columns

The organic pollutants can be steam stripped from a waste water stream by the use of stage contacting devices before discharge. Sieve trays are commonly used devices for stages.

In practice, the feed waste water is normally heated by heat-exchange befor entering the steam stripper. The temperature range could vary (30°C ~ 90°C). It has been reported that the optimum pressure for a minimum steam flow for a packed tower is the vapor prssure of water at the feed temperature (8). In practice, however, the column is normally operated at 1 atmospheric pressure, and the feed enters the column at about 70°C.

For the required removal of an organic pollutant, calculations are performed to obtain is the number of stages required at a steam flow at which column operation is satisfactory.

Any degree of reasonable removal is usually achieved at the mode of column operation associated with the narrow range of the steam flow. Beyond the point where the further increase of the steam flow has a marginal usefulness, the degree of removal is entirely affected by the number of stages.

Steam Stripping without Reflux

The organic pollutants rising in the counter current column as a result of steam stripping are saturated with water vapor. The steam stripper operating without reflux of the aqueous phase produces an overhead vapor which is frequently disposed of by incineration, or is subject to recovery of the organic material through such mans as drying, condensation, selective adsorption, and others.

Even though computers are available for rigorous plate-to-plate solutions of stripping problems, the stripping factor is well suited to the type of the multicomponent waste water streams where the fluctuation of the K - values along the column is negligible or small so that the use of an average value for stripping factor is satisfactory.

$$f = \frac{S^{N+1} - S}{S^{N+1} - 1} \qquad (11)$$

$$x_0 = x_i \left(\frac{S - 1}{S^{N+1} - 1} \right) \qquad (12)$$

where f is the fraction of a given organic pollutant removed by steam stripping, x_o is the effluent concentration which can be expressed in mole fraction, ppm or ppb, xi is the influent concentration which can also be expressed in mole fraction, ppm, or ppb, S is an average stripping factor, KV/L, N is the number of the theoretical stages, V is the vapor flow rate in the stripper, and L is the liquid flow rate in the stripper.

There are a number of design and operating variables which require consideration in applying this method. In addition to the pressure and temperature, it will be necessary to consider the number of stages, composition of the feed, and steam flow rates. In determining the theoretical number of stages for the desired effluent purity, the steam flow beyond the commonly practicable levels (0.0001~ 0.1 kg steam per kg feed) may not be economically practical. The stripping factor in the range of 1 ~ 10 or higher is conducive in approaching the desired separation results.

Also in applying this method, each organic pollutant is treated separately. The stripping of the other organic pollutants is treated individually. The results obtained in this manner can also be used when several organic pollutants are simultaneously stripped in a column.

2. Packed Columns

The stripping of the orgnic pollutants can be carried out in a stage contacting device or in a packed tower. Packed columns have received increased acceptance in pollution control mainly because of the large mass transfer surface area and the cheaper cost for handling corrosive material compared with the stage column.

The design of a packed tower for the desired removal involves the consideration on the packed tower sizing, packing type and size, and packing height. The design should also incorporate liquid distribution and redistribution, packing support, hold-down plate, packing method, special devices, and safety factors.

There are many types of packing that can be used for steam stripping of the organic pollutants from the waste water streams. The factors that need to be considered in choosing a packing are chemical resistance, structural strength, capacity, pressure drop, efficiency, and cost. The stripping efficiency of packing varies with packing size and operating conditions, and generalization is therefore difficult. Larger packing sizes yield greater capacity and lower pressure drop but may give lower efficiency.

Steam Stripping Without Reflux

The application of material balances in combination with the vapor-liquid equilibrium relationship leads to the following expression for the steam stripping operation,

$$\frac{1}{1 - \frac{1}{S}} \ln\left[\frac{x_i}{x_o}\left(1 - \frac{1}{S}\right) + \frac{1}{S}\right] = \frac{Z}{HTU_{ol}} \qquad 13)$$

where x_o is the effluent concentration, x_i is the inluent concentration, S is an average stripping factor KV/L, Z is the packng height, and HTU_{ol} is the height of transfer unit in overall liquid phase units, represented by $L/(K_g aA)$, where A is the empty tower ross-sectional area. The derivation can be found in Reference 28.

3. Steam Stripping with Reflux

The stage or packed steam strlipper can be operted with reflux which recycles the aqueous layer back to the column after phase separation

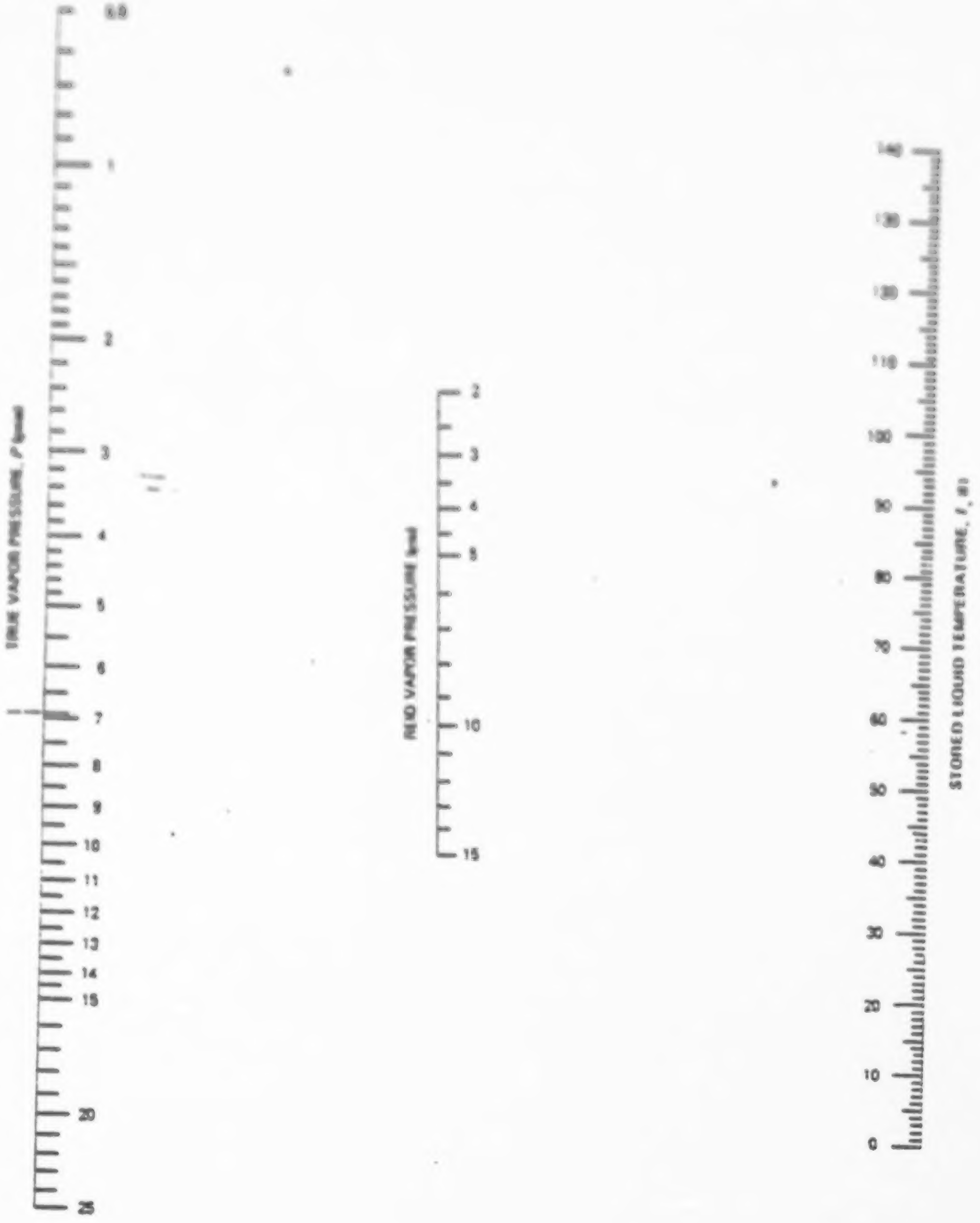


Figure 2. True vapor pressure (P) of crude oils (2-15 psi RVP).

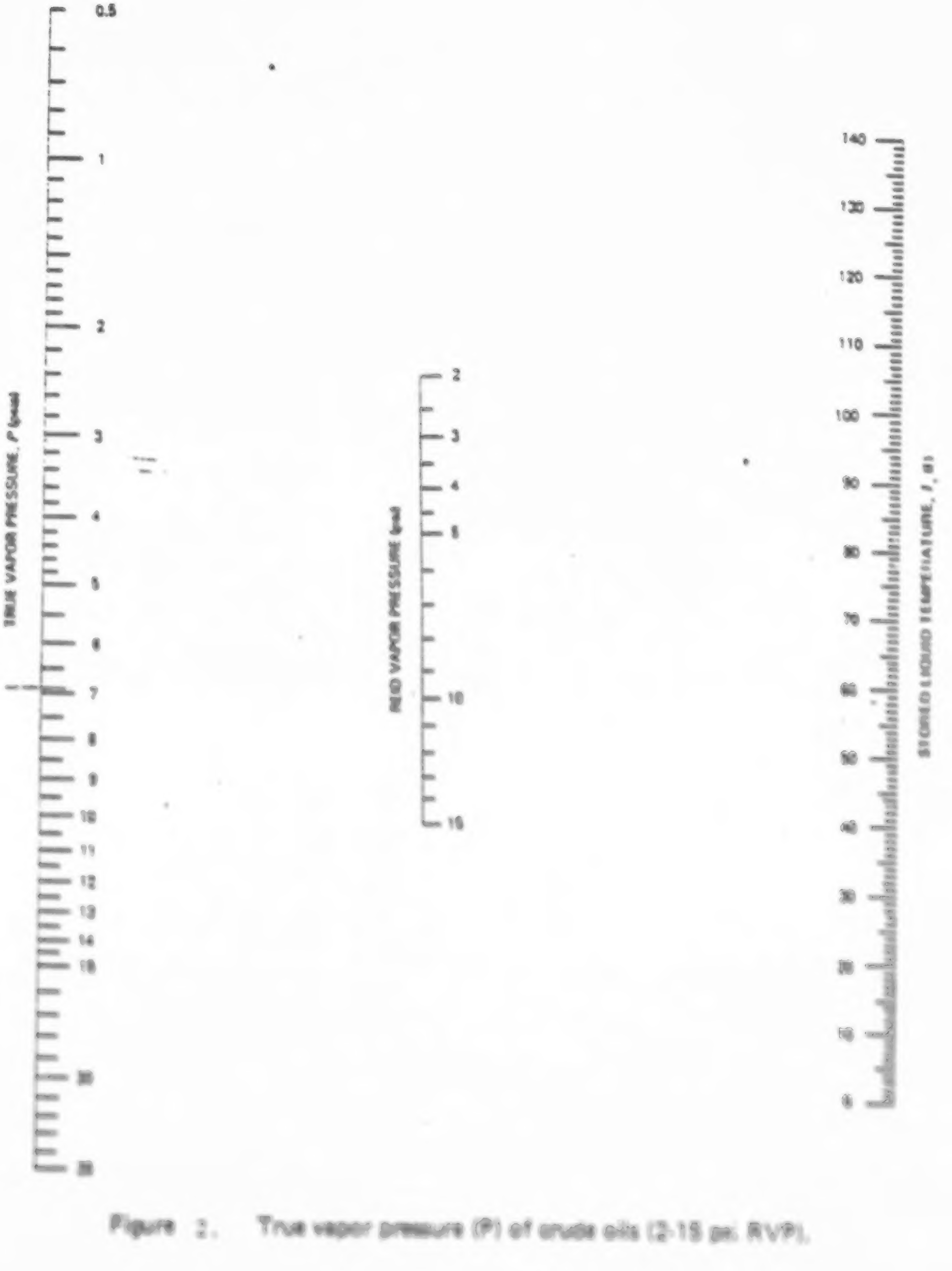
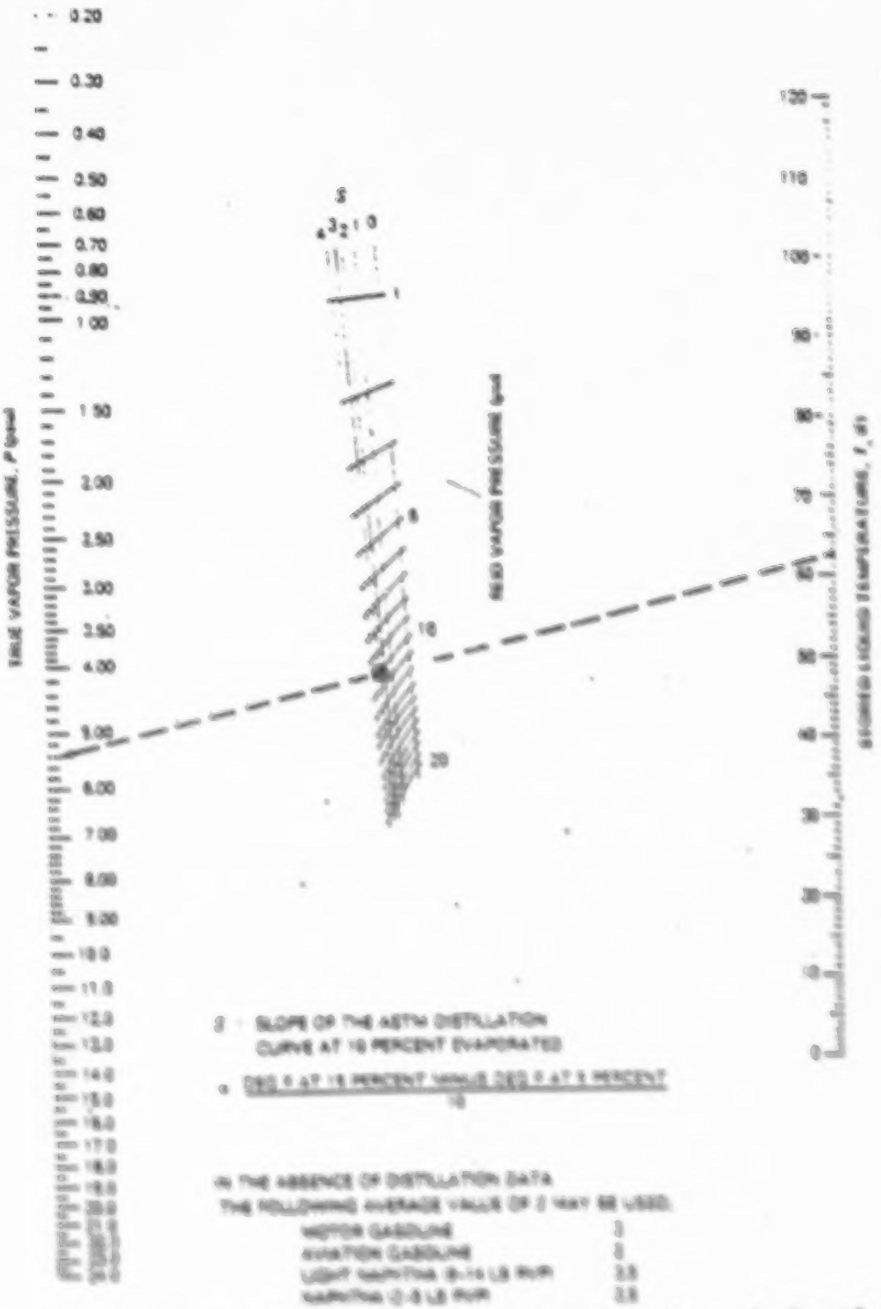


Figure 2. True vapor pressure (P) of crude oils (2-15 psi RVP).



S = SLOPE OF THE ASTM DISTILLATION CURVE AT 10 PERCENT EVAPORATED

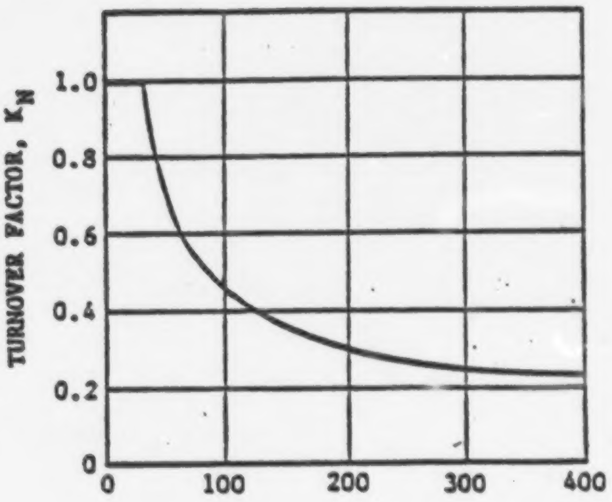
$= \frac{\text{DEG F AT 15 PERCENT MINUS DEG F AT 5 PERCENT}}{10}$

IN THE ABSENCE OF DISTILLATION DATA THE FOLLOWING AVERAGE VALUES OF S MAY BE USED:

MOTOR GASOLINE	3
AVIATION GASOLINE	2
LIGHT NAPHTHA (9-14 LB RVP)	3.5
NAPHTHA (2-8 LB RVP)	2.5

Note: Dashed line illustrates sample problem for RVP = 10 pounds per square inch, gasoline (S = 3), and T_L = 62.5 F (16.9 C). Nomograph drawn from the data of the National Bureau of Standards.

Figure 3. True vapor pressure (P) of refined petroleum liquids like gasoline and naphthas (1-20 psi RVP).



TURNOVERS PER YEAR = $\frac{\text{ANNUAL THROUGHPUT}}{\text{TANK CAPACITY}}$

Note: For 36 turnovers per year or less, K_N = 1.0

Figure 4. Turnover factor (K_N) for fixed roof tanks.

Several methods are used to control emissions from fixed roof tanks. Emissions from fixed roof tanks can be controlled by the installation of a floating roof and seals to minimize evaporation of product being stored. The control efficiency of this method ranges from 60 to 92 percent, depending on the type of roof and seals installed and on the type of organic liquid stored.

A commonly used method, the vapor recovery system, collects emissions from storage vessels and converts them to liquid product. Several vapor recovery procedures may be used, including vapor/liquid absorption, vapor compression, vapor cooling, vapor/solid adsorption, or a combination of these. The overall control efficiencies of vapor recovery systems are as high as 90 to 98 percent, depending on the method used, the design of the unit, the composition of vapors recovered, and the mechanical condition of the system.

A further method of emission control on fixed roof tanks is thermal oxidation. In a typical thermal oxidation system, the air/vapor mixture is injected through a burner manifold into the combustion area of an incinerator. Control efficiencies for this system can range from 96 to 99 percent.

Emission Calculations for External and Internal Floating Roof Tanks: Background Information - The following equation is used to calculate standing storage loss emissions from both external floating roof and internal floating roof storage tanks:

$$L_S = K_S V^N P^* D M_V K_C E_F$$

Where: (1) L_S is the standing storage loss (lb/year)

(2) K_S and N are interdependent factors that relate the type of tank, the design of the tank seal and local wind velocity, V, to standing storage loss

(3) P^*, the vapor pressure function, is a theoretically derived function which establishes the effect of stock volatility on standing storage loss

(4) D, the tank diameter, is linear with standing storage loss as verified [illegible] field tank testing

(5) M_V, the vapor [illegible] weight, provides standing storage loss estim[illegible] mass terms

(6) K_C, the product factor, establishes the relationship of standing storage loss to the type of stored organic liquid

(7) E_F, the secondary seal factor, establishes the effectiveness of secondary seals in controlling standing storage loss

The above factors were developed from emissions data obtained from field and pilot test studies conducted by oil companies, manufacturers, industry groups, and regulatory agencies, on both internal floating roof and external floating roof storage tanks. The largest set of data, concerning external floating roof tanks storing petroleum liquids, was analyzed by the American Petroleum Institute (API), and the results published in Reference 6. The K_S and N values for the primary only and primary/secondary seal systems shown in Table 3 are the same as those published in Reference 6 for seals with "average" gaps.

Due to the small amount of emissions data available for internal floating roof tanks storing volatile organic liquids and petroleum liquids, and external floating roof tanks storing volatile organic liquids, K_S and N factors for these cases were developed from correlations between those available data and the data used to develop the K_S and N values published in Reference 6. These correlations were used to develop K_S and N factors for

TABLE 3. SEAL RELATED FACTORS FOR EXTERNAL FLOATING ROOF TANKS[a,b]

Seal Type	K_S	N
Metallic Shoe Seal		
Primary seal only	1.2	1.5
With shoe mounted secondary seal	0.8	1.2
With rim mounted secondary seal	0.2	1.0
Liquid Mounted Resilient Seal		
Primary seal only	1.1	1.0
With weather shield	0.8	0.9
With rim mounted secondary seal	0.7	0.4
Vapor Mounted Resilient Seal		
Primary seal only	1.2	2.3
With weather shield	0.9	2.2
With rim mounted secondary seal	0.2	2.6

[a] Based on emissions from tank seal system with emissions control devices (roof, seals, etc.) in reasonably good working condition, no visible holes, tears or unusually large gaps between the seals and the tank wall.

[b] Factors for secondary seals are appropriate only for external floating roof tanks storing petroleum liquids.

primary seal only cases. Analysis of the available test data shows the secondary seal control efficiency to range from 55 to 93 percent. Based on this information, the secondary seal factor, E_F, was developed. For correct application of the secondary seal factor, a visual inspection of the tank and seal of interest is suggested. If the tank and seal are found in good condition (no tears or holes in the seal and no apparent large gaps at the tank wall/seal junction), a value of E_F = 0.25 (75 percent control efficiency) is recommended.

Further analysis of all available data shows that, for any seal system, emissions from tanks storing volatile organic liquids were generally ten times those of the same tank type storing petroleum liquids. Based on this information, the value of the product factor, K_C, was determined to be 10 for tanks storing volatile organic liquids.

Due to the small amount of data available, the method and factors used to calculate standing storage loss emissions from external floating roof tanks storing volatile organic liquids, and internal floating roof tanks storing both petroleum liquids and volatile organic liquids, are considered interim methods, awaiting further data development.

External Floating Roof Tank Standing Storage Loss Calculations[6] - The standing storage loss from external floating roof tanks can be estimated from the following equation:

$$L_S = K_S V^N P^* D M_V K_C E_F \qquad (6)$$

Where: L_S = standing storage loss (lb/yr)

K_S = seal factor (lb-mole/(ft (mi/hr)^{N}yr)). See Note 1

V = average wind speed at tank site (mi/hr). See Note 2

N = seal related wind speed exponent (dimensionless). See Note 1

P^* = vapor pressure function (dimensionless). See Note 3

$$= \frac{\left(\frac{P}{P_A}\right)}{\left[1 + \left(1 - \frac{P}{P_A}\right)^{0.5}\right]^2}$$

P = true vapor pressure at average actual organic liquid storage temperature (psia)

P_A = average atmospheric pressure at tank location (psia)

D = tank diameter (ft)

M_V = average vapor molecular weight (lb/lb-mole). See Note 4

K_C = product factor (dimensionless). See Note 5

E_F = secondary seal factor. See Note 6

Notes: (1) For petroleum liquid storage: K_S and N for both primary only and primary/secondary seal systems are found in Table 3.

For volatile organic liquid storage: only the K_S and N values of Table 3 for the primary only seal systems are employed. If the storage tank of interest has both a primary and secondary seal, use the K_S and N value for the particular primary seal of interest and the appropriate E_F value. See Note 6

(2) If the wind speed at the tank site is not available, wind speed data from the nearest local weather station may be used as an approximation

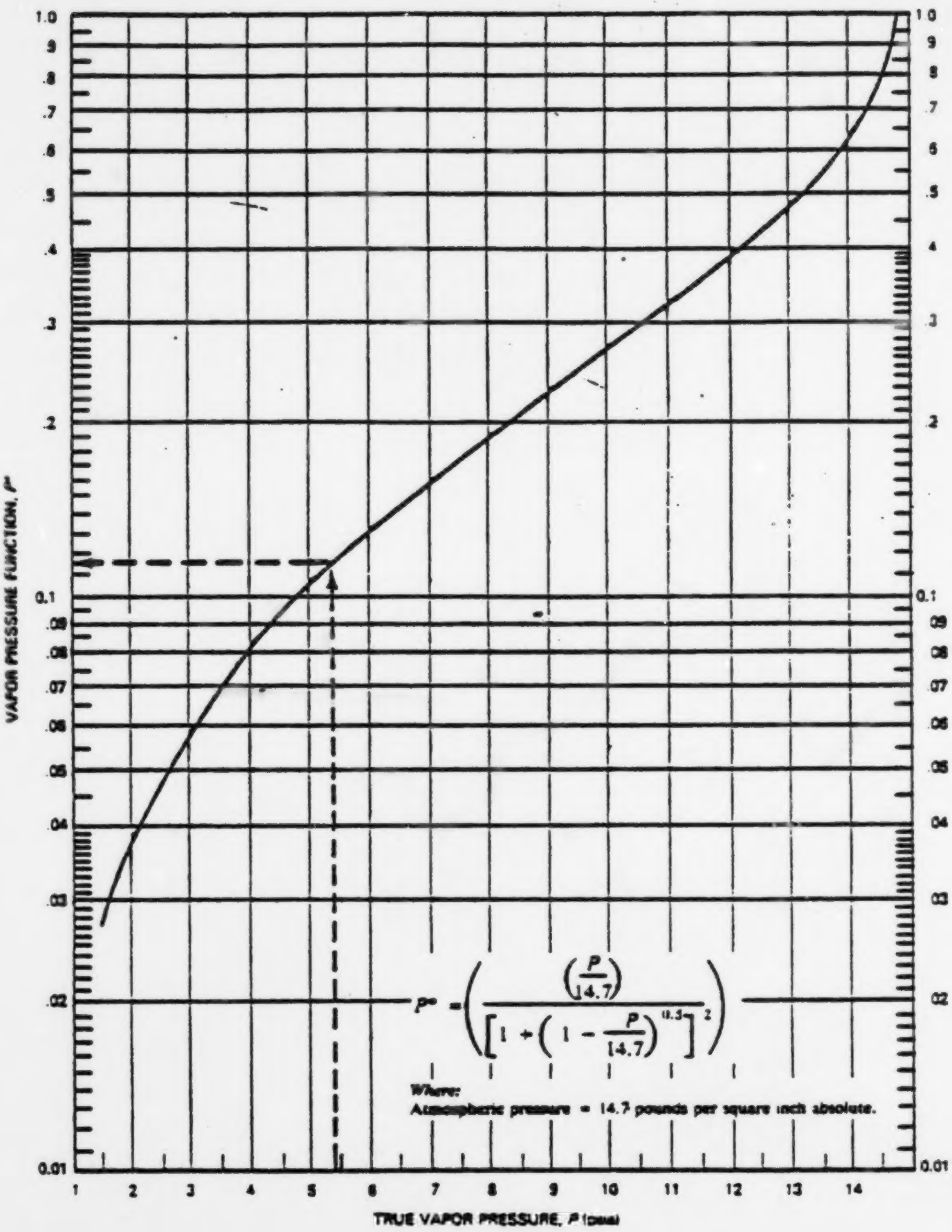
(3) P^* can be calculated or read directly from Figure 5. True vapor pressures for organic liquids can be determined from Figures 2 or 3, or Table 1. If average actual organic liquid storage temperature, T_S, is unknown, the average storage temperature can be estimated from the average ambient temperature T_A(F) (available from local weather service data), adjusted by the tank paint color factor. See Table 4.

(4) The molecular weight of the vapor, M_V, can be determined by Table 1, analysis of vapor samples, or by calculation from the liquid composition. A typical value of 64 lb/lb-mole can be assumed for gasoline, and a value of 50 lb/lb-mole can be assumed for U.S. midcontinental crude oils

(5) For all petroleum liquids except crude oil: $K_C = 1.0$
For crude oil: $K_C = 0.4$
For all volatile organic liquids: $K_C = 10.0$

(6) For petroleum liquid storage with
any seal system: $E_F = 1.0$
For volatile organic liquid storage
with a primary only seal system: $E_F = 1.0$
with a primary/secondary seal system: $E_F = 0.07\text{-}0.45$

(A value of 0.25 is recommended for tanks and seals in good condition.)



NOTE: Dashed line illustrates sample problem for $P = 5.4$ pounds per square inch absolute.

Figure 6. Vapor pressure function (P*). 6

TABLE 4. AVERAGE STORAGE TEMPERATURE (T_S) AS A FUNCTION OF TANK PAINT COLOR[a]

Tank color	Average storage Temperature, T_S (F)
White	$T_A + 0$
Aluminum	$T_A + 2.5$
Gray	$T_A + 3.5$
Black	$T_A + 5.0$

[a] Reference 6.

Internal Floating-Roof Tank Standing Storage Loss Calculations – Standing storage loss emissions from internal floating roof tanks are best estimated from Equation 6:

where: K_S = 0.7 for all seal systems

N = 0.4 for all seal systems

K_C = 1.0 for petroleum liquid storage

K_C = 10.0 for volatile organic liquid storage

E_F = 1.0 for primary only seal systems

E_F = 0.07 - 0.45 for primary/secondary seal systems (A value of 0.25 is recommended for tanks and seals in good condition.)

Withdrawal Loss from External Floating Roof and Internal Floating Roof Storage Tanks[6] – The withdrawal loss from external floating roof and internal floating roof storage tanks can be estimated using Equation 7.

$$L_W = \frac{(0.943)QCW_L}{D} \qquad (7)$$

Where: L_W = withdrawal loss (lb/yr)

Q = average throughput (barrel (bbl)/yr; 1 bbl = 42 U.S. gallons)

C = shell clingage factor (bbl/1000 ft^2). See Table 5

W_L = average organic liquid density (lb/gal). See Note 1

D = tank diameter (ft).

Notes: (1) If W_L is not known, an average value of 6.1 lbs/gallon can be assumed for gasoline. An average value cannot be assumed for crude oil, since densities are highly variable

(2) The constant, 0.943, has dimensions of (1000 ft^3 x gal/bbl^2)

Total Loss from External Floating Roof and Internal Floating Roof Storage Tanks[6] - The total loss from external floating roof and internal floating roof storage tanks in lb/yr can be estimated from Equation 8.

$$L_T(\text{lb/yr}) = L_S(\text{lb/yr}) + L_W(\text{lb/yr}) \qquad (8)$$

Where: L_T = total loss

L_S = standing storage loss

L_W = withdrawal loss

TABLE 5. AVERAGE CLINGAGE FACTORS (C) (bbl/1000 ft^2)[a]

	Shell Condition		
Product	Light rust	Dense rust	Gunite lined
Gasoline	0.0015	0.0075	0.15
Crude oil	0.0060	0.030	0.60

[a] Reference 6.

Vapor Phase Concentration of a Specific Chemical

The concentration of a component i in the vapor phase in equilibrium with stored liquid can be represented rigorously by a thermodynamic relationship

$$y_i = \frac{\gamma_i f^o_{iL}}{\phi_i P} x_i \qquad (9)$$

where y_i : mole fraction of component i in the vapor phase

x_i : mole fraction of component i in the liquid phase

f^o_{iL}: fugacity of component i in the liquid phase at system temperature and pressure at a defined standard state which is normally taken as the pure component at the temperature and the pressure of the mixture.

ϕ_i : fugacity coefficient of component i in the vapor mixture.

γ_i : activity coefficient of component i in liquid solution.

P : total pressure.

For hydrocarbon mixtures, Chao-Seader(8) presented a correlation for determining the vapor-liquid equilibrium constant, K_i, by expressing f^o_{iL} in terms of the fugacity coefficient of pure liquid component i at system conditions(ν^o_i), or $f^o_{iL} = \nu^o_i P$, to get

$$y_i = K_i x_i \qquad (10)$$

where

$$K_i = \frac{\gamma_i \nu^o_i}{\phi_i}$$

At modest pressures which may be encountered in normal storage conditions, the fugacity coefficient is close to unity and the liquid phase, standard state fugacity approaches the vapor pressure at system temperature. Hence the vapor-liquid equilibrium constant in Equation (10) can be represented by

$$K_i = \gamma_i P^o_i / P. \qquad (11)$$

When a multicomponent mixture containing many soluble compounds, organic or inorganic, is stored, Equation (11) is applicable as long as the activity coefficient is evaluated in a proper manner. The activity coefficient can be determined from many empirical-theoretical correlations as well as experimental data(17).

Since most multicomponent vapor-liquid equilibrium data are often unavailable, there are several methods of calculating the activity coefficient for multicomponent mixtures from data on the constituent binary pairs. The mathematical expressions using binary parameters serve a useful purpose of predicting multicomponent phase equilibria beyond the range covered by the experimental measurements.

Among these are the expressions developed by Van Laar (9), Margules (10), Wilson (11), Renon (12), Deal (15), and more recently UNIQUAC (13) and UNIFAC (14).

For hydrocarbons in aqueous solution, Prausnitz presented several semi-empirical correlations(16). If the solubility of an organic compound in water is small, the activity coefficient can be determined by

$$\gamma_i = \frac{1}{x_i} \tag{12}$$

where x_i is the solubility of component i expressed in mole fraction.

When Raoult's law holds as is often the case for hydrocarbon mixtures, it can be assumed that the activity coefficient is close to unity.

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Waste Piles

Handling, treatment, or storage of non-containerized solid hazardous wastes inherently requires maintenance of outdoor waste piles. Waste piles are usually left uncovered, partially because of the necessity for frequent transfer of material into or out of the pile.

Dust emissions occur at several points in the storage cycle - during loading of material onto the pile, during disturbances by strong wind currents, and during loadout of material from the pile. The movement of trucks and loading equipment in the waste pile area is also a substantial source of dust emissions. The method of estimating dust emissions from waste piles is taken from AP-42 and its recommended procedure for "Aggregate Storage Piles."

1. Emissions and Correction Parameters - The quantity of dust emissions from aggregate waste pile operations varies linearly with the volume of aggregate passing through the storage cycle. In addition, emissions depend on the following correction parameters that characterize the condition of a particular waste pile: (1) age of the pile, (2) moisture content, and (3) proportion of aggregate fines.

When freshly processed aggregate is loaded onto a waste pile, its potential for dust emissions is at a maximum. Fines are easily disaggregated and released to the atmosphere upon exposure to air currents resulting from aggregate transfer or high winds. As the aggregate weathers, however, the potential for dust emissions is greatly reduced. Moisture causes aggregation and cementation of fines to the surfaces of larger particles. Any significant rainfall soaks the interior of the pile, and the drying process is very slow.

2. Corrected Emission Factor - Total dust emissions from aggregate waste piles can be divided into the contributions of several distinct source activities that occur within the storage cycle:

a. Loading of aggregate onto waste piles.

b. Equipment traffic in storage area.

c. Wind erosion.

d. Loadout of aggregate for shipment.

Table 1 shows the emissions contribution of each source activity, based on field tests of suspended dust emissions from crushed stone and sand and gravel piles. A 3-month storage cycle was assumed in the calculations.

Table 1 - Aggregate Waste Pile Emissions

Source activity	Correction Parameter	Approximate percentage of total
Loading onto piles	PE index[a]	12
Vehicular traffic	Rainfall frequency	40
Wind erosion	Climatic factor	33
Loadout from piles	PE index[a]	15
Total		100

[a] Thornthwaite's precipitation-evaporation index.

Also shown in Table 1 are the climatic correction parameters that differentiate the emissions potential of one aggregate storage area from another. Overall, Thornthwaite's precipitation-evaporation index best characterizes the variability of total emissions from aggregate waste piles.

The quantity of suspended dust emissions from aggregate waste piles, per ton of aggregate placed in storage, may be estimated using the following empirical expression[1]:

$$E = \frac{0.33}{\left(\frac{PE}{100}\right)^2} \qquad (1)$$

where: E = Emission factor, pounds per ton placed in storage.

PE = Thornthwaite's precipitation-evaporation index (see (Figure 1).

Equation 1 describes the emissions of particles less than 30 um in diameter. This particle size was determined[1] to be the effective cutoff diameter for the capture of aggregate dust by a standard high-volume filtration sampler, based on a particular density of 2.0-2.5 g/cm^3. Because only particles smaller than 30 um are included, equation 1 expresses the total emissions likely to remain indefinitely suspended. (See section 11.2.1.3 of AP-42(1)).

3. Control Methods - Watering and use of chemical wetting agents are the principal means for control of aggregate waste pile emissions. Watering is useful mainly to reduce emissions from vehicular traffic in the waste pile area. Frequent watering can, based on the breakdowns shown in Table 1, reduce total emission by about 40 percent. Watering of the waste piles themselves typically has only a very temporary, minimal effect on total emissions. A much more effective technique is to apply chemical wetting agents to provide better wetting of fines and longer retention of moisture film. Continuous chemical treatment of

material loaded onto piles, coupled with watering of treatment of roadways, can reduce total particulate emissions from aggregate storage operations by up to 90 percent (1).

1. Compilation of Air Pollutant Emission Factors (AP-42), U.S. Environmental Protection Agency, Research Triangle Park, N.C., December 1981.

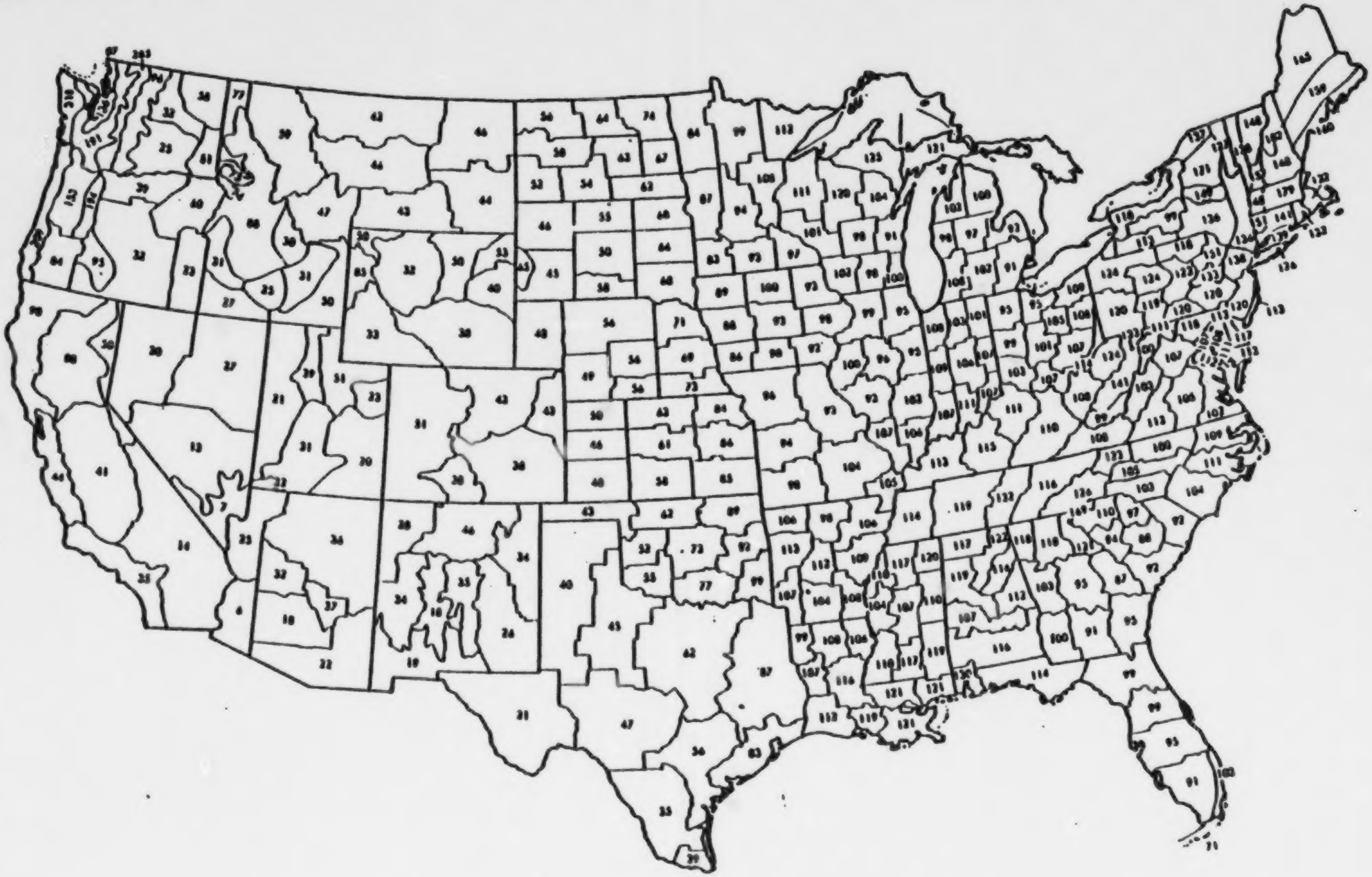

Figure 1. Map of Thornthwaite's Precipitation-Evaporation Index values for state climatic divisions

Emissions from Pan Evaporation

Equations for predicting the emission rate of volatile chemicals from water basins at ambient temperatures have been developed (1). The emission rate of volatile chemicals i, N_i (mol/hr·m^2), in water (chemical j) at low mass-transfer rates can be quantified by:

$$N_i = K_{Li} (x_i - x_i^*) \qquad (1)$$

where K_{Li} is the overall liquid phase mass-transfer coefficient, mol/hr·m^2, x_i is the mole fraction of chemical i in water, and x_i^* is the mole fraction of i in water in equilibrium with mole fraction in the air, y_i.

The overall coefficient is a function of the individual phase coefficient for water, k_{Li}(mol/hr·m^2), for air k_{Gi}(mol/hr·m^2), and Henry's law constant in mole fraction form(i.e., $y_i = K_i \, x_i$):

$$\frac{1}{K_{Li}} = \frac{1}{k_{Li}} + \frac{1}{K_i \, k_{Gi}} \qquad (2)$$

In the case of large K_i values, $K_{Li} = k_{Li}$, and the liquid phase controls the mass transfer rate. For low K_i values, $K_{Li} = K_i \, k_{Gi}$, and the gas phase controls.

In the case of chemical desorption at high mass-transfer rates, Equation (1) is inadequate. The high rate of water flux, N_j (mol/hr·m^2), during thermal evaporation destorts the concentration profiles near the interface and effects the magnitude of the transport coefficients (2). If the liquid phase controls the rate of mass transfer, the film-theory rate equation with $x_i^* = 0$ is:

$$N_i = \frac{N_i}{N_i + N_j} k_{Li} \ln \frac{N_i/(N_i+N_j) - 0}{N_i/(N_i+N_j) - x_i} \qquad (3)$$

The water evaporation rate is much larger than that of chemical i; $N_j >> N_i$. For this condition Equation (3) transforms to:

$$N_i = N_j \, x_i \frac{\exp(N_j/k_{Li})}{\exp(N_j/k_{Li}) - 1} \qquad (4)$$

If $N_i/k_{Li} \geq 3$, the rate of loss of chemical i is controlled by the water evaporation rate, N_j, and the mole fraction of chemical i in the water, x_i.

Laboratory experiments for studying thermal evaporative emissions are conveniently performed batchwise. A quantity of water, M_j^o(mols), with chemical content x_i^o, is placed in an appropriate pan or flask and heated. The transient behavior is:

$$x_i = x_i^o \left(\frac{M_j^o - A\,N_j\,t}{M_j^o}\right)^{\frac{K_{Li} - N_j}{N_j}} \qquad (5)$$

where A is the air-water interfacial area, (m^2), of the evaporator. In the case of a round-bottom flask-type evaporator, A is a function of M_j and this variability must be accounted for in N_j determinations. Equation (5) suggests that if $K_{Li} = N_j$, then x_i in the evaporator is constant and independent of time.

The experimental data and theory suggest that the appropriate rate equation for determining emission rates of toxic chemicals at thermal evaporation conditions of high water evaporation rate is (2):

$$N_i = N_j \, x_i \qquad (6)$$

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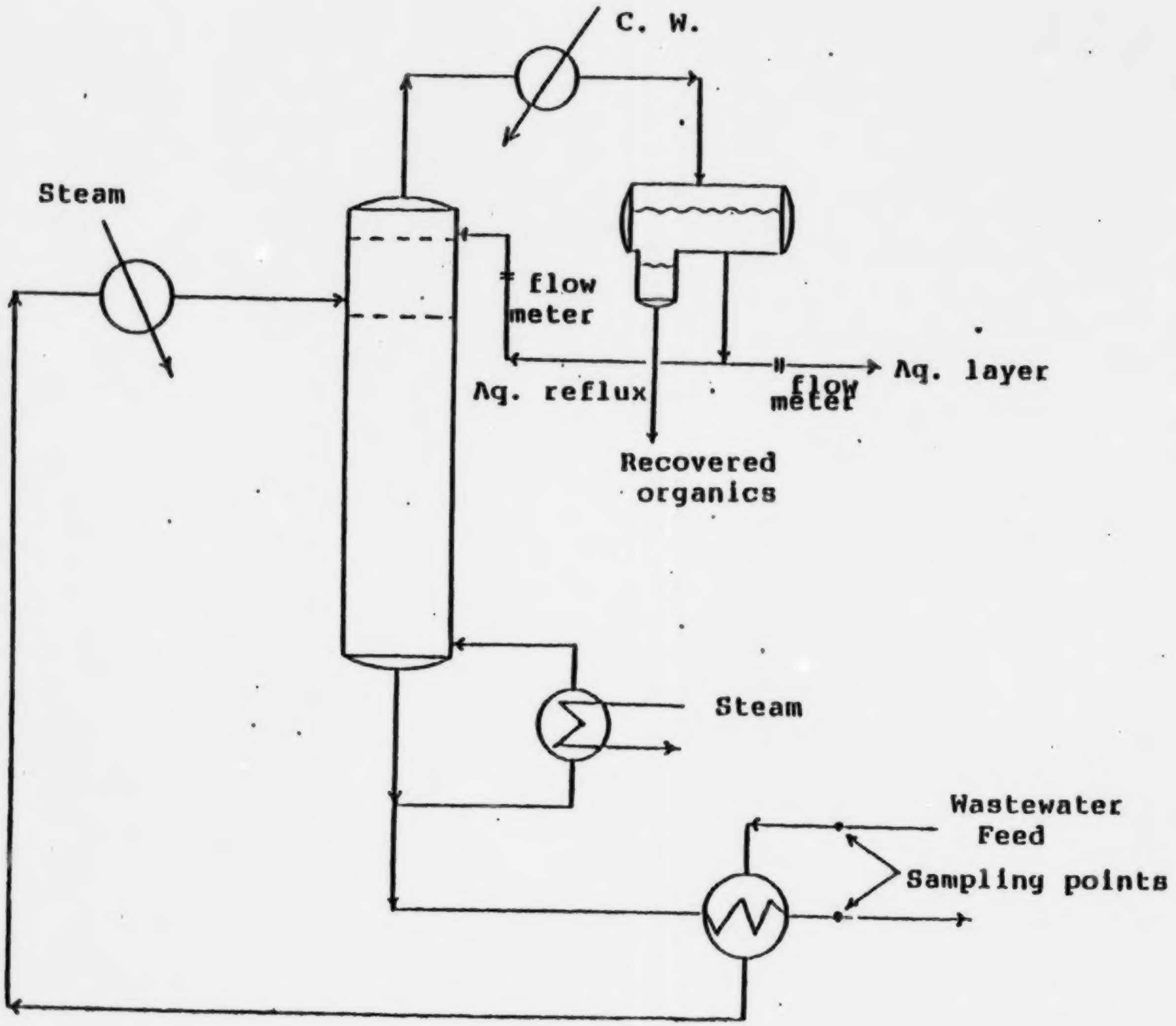
Figure 1. Wastewater Steam Stripper Schematic


C. W.
Steam
flow meter
Aq. reflux
flow meter
Aq. layer
Recovered organics
Steam
Wastewater Feed
Sampling points

of the condensed overhead. Figure (1) is a schematic of the operation. The organics can be recoverd from the top or from the bottom of the aqueous layer. This mode of operation offers an advantage of recovering the organic materials as liquid and increasing the degree of removal for volatile organic pollutants. However, ther are certain operability limitations associated with refluxing mode of operation.

Refluxing of the overhead condensate is commonly employed in the practice of industrial distilltion to improve the degree of separation. The difference here is that the overhead condensate is the two phase system as normally encountered in azeotropic distillation. An expression for describing the steam stripper with reflux can be found in Reference 28.

The amount of steam flow is important on the operability of the refluxing mode. As the steam flow is increased the column overhead vapor will contain a proportionately high content of water vapor. the prudent adjustment of steam flow will achieve the desired results of two phase separation related to the mutual solubility limitations. Excessive use of steam will result in non-formation of organic layer, and the operation will be essentially non-workable.

C. Tray Efficiencies

The number of theoretical stages obtained in Section (B) must be divided by the stage efficiency to obtain the number of actual stages required for the desired removal. The methodology is described below. Since tray efficiencies are expressed in several ways, the definition of them is important.

1. Definition of Tray Efficiencies

a. Overall Column Efficiency

The overall column efficiency E_o is the ratio of the number of theoretical stages required to the number of actual stages required to make a separation.

b. Murphree Stage Efficiency

The Murphree stage efficiency or plate efficiency is defined as

$$E_{mv} = \frac{y_n - y_{n+1}}{y_n^* - y_{n+1}} \qquad (14)$$

where y_n^* means the vapor composition in equilibrium with the liquid leaving the nth stage, and y_n and y_{n+1} are the vapor compositions leaving the nth and n+1st stages, respectively. In this situation, it is assumed that the inlet and outlet vapors and the liquid on the stage are well mixed.

c. Point Efficiency

The point efficiency refers to the efficiency at a single point on a stage, and is defined as

$$E_{OG} = \frac{y - y_{n+1}}{y^* - y_{n+1}} \qquad (15)$$

where y differentiates from y_n to denote the variation of the concentration in the direction of the liquid flow.

The point efficiency can be expressed in terms of overall gas-phase transfer units N_{OG} by application of the standard mass transfer equation.

$$E_{OG} = 1 - e^{-N_{oG}} \qquad (16)$$

2. Relationship between Tray Efficiencies

The derivation relating overall column efficiency, Murphree stage efficiency, and point efficiency is given elsewhere (3). The results for the intermediate case where partial mixing of the liquid occurs, which are used for the present analysis, are summarized below.

$$\frac{E_{mv}}{E_{OG}} = \frac{1 - e^{-(\eta + P_e)}}{(\eta + P_e)(1 + (\eta + P_e)/\eta)} + \frac{e^{\eta} - 1}{\eta(1 + \eta/(\eta + P_e))} \qquad (17)$$

where

$$\eta = \left(\frac{P_e}{2}\right)\left(\sqrt{1 + \frac{4\ S\ E_{OG}}{P_e}} - 1\right)$$

$$P_e = \frac{Z_L^2}{D_E\ \theta_L}$$

D_E is the eddy diffusion coefficient, Z_L is the length of liquid travel across tray, θ_L is the liquid residence time on tray, P_e is the Peclet number, and S is the stripping factor.

$$E_a = \frac{E_{mv}}{1 + E_{mv}\ (e/(1-e))} \qquad (18)$$

where e refers to the weight fraction of the net liquid that is entrained, and E_a refers to the plate efficiency obtained in the presence of entrainment.

$$E_O = \frac{\ln\ [1 + E_a\ (S - 1)]}{\ln\ S} \qquad (19)$$

The chart giving the values of E_{mv}/E_{og} at various P_e and $S \cdot E_{OG}$ values(13) was utilized instead of manual calculations using Equation (17).

3. Correlations

The correlations for predicting the number of transfer units for use in Equation (26) are mostly done empirically. The A.I.Ch.E methods applicable to sieve trays are (11) (14) modified by Hwang based on data obtained using commercial columns (29). The experimental results are.

$$N_{tG} = \frac{18.52 + 108.07\ h_w - 5.67\ V_a\ \rho_G^{0.5} + 2497\ q/z}{S_{cG}^{0.5}} \qquad (20)$$

$$N_{tL} = 1.368 \times 10^3\ D_L^{0.5}\ (0.213\ V_a\ \rho_G^{0.5} + 0.15)\ \theta_L \qquad (21)$$

Other correlations needed to calculate tray efficiences include:

$$D_E = (3.776 \times 10^{-3} + 0.0171\ V_a + 3.671\ q/z + 0.18\ h_w)^2 \qquad (22)$$

$$\theta_L = \frac{h_L\ Z_L}{q/z} \qquad (23)$$

$$h_L = 0.0419 + 0.19\ h_w - 0.0135\ V_a\ \rho_G^{0.5} + 2.452\ q/z \qquad (24)$$

and the use should be made of the relationship

$$\frac{1}{N_{oG}} = \frac{1}{N_{tG}} + \frac{KV}{L}\ \frac{1}{N_{tL}} \qquad (25)$$

Equations (20) through (25) should be applicable to bubble-cap trays as well. For sieve or perforated trays, Equation (24) for the liquid hold-up should be replaced by the expression taken from the correlation of Gerster (5),

$$h_L = 0.0061 + 0.725\ h_w - 0.238\ h_w V_a\ \rho_G^{0.5} + 1.225\ q/z \qquad (26)$$

The recommended procedure for predicting tray efficiencies is as follows:

1. Calculate N_{tG} using Equation (20). (The resistence due to N_{tG} is small for the dominant liquid-phase resistance).
2. Evaluate h_L by Equation (24), then θ_L by Equation (23), and then calculate N_{tL} by Equation (21).
3. Calculate N_{OG} from the values of N_{tG}, N_{tL} and the vapor-liquid equilibrium constant using Equation (25).
4. Determine D_E from Equation (22), and the ratio E_{mv}/E_{OG} using Equation (17).
5. Calculate E_{OG}, E_{mv}, E_a and E_O, using Equations (16), (17), (18), and (19) respectively.

4. Packing Efficiency

The method of relating the height of transfer unit to the column performance in terms of the number of transfer unit and the packing height is previously presented (8). The Sherwood-Holloway correlation for the height of a liquid phase transfer unit takes the form.

$$H_L = \beta \left(\frac{G_L}{\mu_L} \right)^{\alpha} (Sc_L)^{0.5} \qquad (27)$$

The coefficients for various packings are shown in Table 3 (29).

Table 3. Coefficients in the correlation given by Equation (27)

Packing Material	β	α
5/8" polypropylene Pall Rings	0.000953	0.427
1" polypropylene Pall Rings	0.002	0.36
2" Ceramic Raschig Rings	0.0026	0.32
2" Ceramic Intalox	0.00139	0.36
3" Kynar Tellerettes	0.00294	0.37

Example: A wastewater containing a wide range of volatile toxic chemicals is to be steam stripped using a 3 foot diameter valve-tray column with 18 trays for stripping. Calculate the concentration of benzene after steam stripping the waste containing 5000 ppm of benzene. The tray data are as follows:

h_w = 0.0508 m (2")

z = 1.41 m (4.625 ft)

Z_1 = 1.537 m (5.044 ft)

D_L = 4.568×10^{-9} m^2/s for benzene

A_a = 26.15 ft^2

liquid flow = 116.5 gpm

steam flow = 22,000 lbs./hr

stripping factor = 432 for benzene

The use of the procedure outlined previously for calculating the tray efficiencies will yield E_O = 0.13%, E_{mv} = 0.17% and E_O = 8.9%. Hence the theoretical number of trays for stripping is 18 X 0.089 = 1.6 trays. From Equation (12), one gets

$$x_o = 5000 \frac{432 - 1}{432^{1.6+1} - 1} = 0.3 \text{ ppm}$$

The concentration of benzene in the waste after steam stripping will be 0.3 ppm.

NOTATION

A,B = constants in Equation (5)

A = empty tower cross-sectional area, m^2

D_E = eddy phase diffusion coefficient, m^2/s

D_L = liquid phase diffusion coefficient m^2/s

e = weight fractionof the net liquid that is entrained

E_a = Murphree efficiency corrected by entrainment

E_{mv} = Murphree stage efficiency

E_o = overall column eficiency

E_{oG} = point efficiency

f = fraction of dissolved solute removed

G_L = liquid loading, $kg/s \cdot m^2$

H = Henry's Law constant, m^3 atm/mol

H_L = height of a liquid phase transfer unit, m

HTU_{oL} = height of an overall liquid pahse transfer unit, m

h_L = hydraulic head on a tray, m

h_w = weir height, m

K = slope of equilibrium curve

$K_x a$ = overall liquid phase mass-transfer coefficient, $kg/(m^3 \cdot s)$

L = superficial liquid rate, kg/s

N = number of theoretical stages

N_{OG} = number of overall gas phase transfer unit

N_{tG} = number of gas-phase transfer unit

N_{tL} = number of liquid-phase transfer unit

P = total pressure, Pa

P^o = vapor pressure, Pa

q = rate of liquid flow, m^3/s

I.D.	Compound	Tricresyl Phosphate	Undecane	HIBK	Tridecane	Benzene	Isobutylene	Isobutane	n butyl acetate	Isobutyl acetate	Di isopropyl ether	Octan
51.	chlorodibromomethane	30*	28*	140*	26*	120*	53*	32*	140*	130*	34*	173*
52.	hexachlorobutadiene	288**	90*	270*	59*	9500*	180*	86*	280*	240*	140*	299*
53.	hexachlorocyclopentadiene	26000*	25000*	40560*	20900*	86000*	52000*	34000*	36900*	37600*	37000*	2.4×10^{4}*
54.	isophorone	42*	28*	86*	24*	150*	46*	29*	85*	79*	43*	78*
55.	naphthalene	2600**	830*	2160*	590*	17400*	2070*	1220*	2100*	2000*	1700*	2344$^{(9)(11)(}$
56.	nitrobenzene	61**	55*	250*	47*	460*	72*	44*	260*	230*	97*	71$^{(9)}$,(
57.	2-nitrophenol	52***	1**	185***	1**	213.8$^{(9)}$	3.8**	0.9**	140***	157***	60***	40$^{(9)}$
58.	4-nitrophenol	39***	0.6**	137***	0.6**	1.3$^{(9)}$	1.7**	0.4**	74***	116***	44***	81$^{(9}$
59.	2, 4-dinitrophenol	101***	22$^{(9)}$	360***	22***	10***	14**	4**	272***	303***	117***	240$^{(9}$
60.	4,6-dinitro-o-cresol	382***	31***	1360***	31***	31***	94***	24***	1028***	1146***	441**	708$^{(1}$
61.	N-nitrosodimethylamine	0.13**	0.1*	0.3*	0.1*	0.2*	0.16*	0.1*	0.3*	0.3*	0.1*	0.24$^{(1}$
62.	N-nitrosodiphenylamine	635**	260*	1600*	180*	3900*	1200*	630*	1450*	1380*	600*	620*
63.	N-nitrosodi-n-propylamine	17**	18*	66*	16*	64*	34*	22*	64*	60*	24*	22$^{(1}$
64.	pentachlorophenol	15466***	100***	54000***	100***	2900***	540***	140***	41570***	46000***	17850***	$1\times10^{5(9)}$
65.	phenol	20$^{(7)}$	0.14$^{(9)}$	71$^{(7)}$	0.14$^{(9)}$	2.26$^{(7)(9)}$	0.42$^{(7)}$	0.11$^{(7)}$	38$^{(9)}$ – 53.8$^{(4)}$	60$^{(7)}$	23$^{(7)}$	30$^{(9)}$

I.D.	Compound	Cumene	Mesityl oxide	MEK	ethyl acetate	Ethyl ether	Ethyl benzene	n-hexanol	EDC	Toluene	Xylene	n-hexane
51.	chlorodibromomethane	41.*	197*	272*	237*	88*	104*	250*	41*	115*	183*	37*
52.	hexachlorobutadiene	1430*	232*	158*	135*	227*	3000*	40*	2.3x10^4*	4340*	4976*	277*
53.	hexachlorocyclopentadiene	5.5x10^4*	3.6x10^4*	4x10^4*	3.6x10^4*	5.8x10^4*	60,000*	1x10^4*	6.2x10^4*	69000*	975000*	4.7x10^4*
54.	isophorone	87*	95*	111*	95*	80*	102*	53*	120*	116*	174*	47*
55.	naphthalene	5870*	1820*	1440*	1320*	2300*	7700*	.334*	2.6x10^4*	1x10^4*	1.25x10^4*	2100*
56.	nitrobenzene	246*	309*	349*	298*	176*	309*	270*	353*	363*	550*	80*
57.	2-nitrophenol	63***	97***	112***	153***	151(9)	100**	75***	13***	190.5(9)	199.5(9)	0.9**
58.	4-nitrophenol	46***	72***	83***	113***	109.5(9)	1.2**	56***	6.2(9)	1.2**	1.2**	0.006(9)
59.	2, 4-dinitrophenol	120***	187***	217***	296***	200***	4***	146***	15***	8***	4***	3.5(9)
60.	4,6-dinitro-o-cresol	460***	707***	820***	1120***	756***	10***	550***	107***	30***	10***	25***
61.	N-nitrosodimethylamine	0.13*	0.42*	0.54*	0.49*	0.24*	0.16*	0.46*	0.13*	0.18*	0.29*	0.12*
62.	N-nitrosodiphenylamine	1286*	2028*	3600*	3040*	1790*	1722*	284*	3500*	1800*	2900*	881*
63.	N-nitrosodi-n-propylamine	33*	74*	90*	80*	58*	49*	37*	36*	55*	82*	28.*
64.	pentachlorophenol	18000***	28000***	33000***	45000***	30600 ***	4000***	22000***	16500***	1800***	1400*	141(9)
65.	phenol	.24**	37**	43**	58.6(3)	39.6(3)	3.1*	28.8(9)	5.06(3)	1.4(3)(9)	1.1(3)(9)	0.11(3),(

I.D.	Compound	Tricresyl Phosphate	Undecane	MIBK*	Tridecane	Benzene	Isobutylene
66.	bis(2-ethylhexyl) phthalate	2.7×10^{10}**	4×10^{9}**	6.7×10^{10}**	2.3×10^{9}**	3×10^{11}**	1×10^{10}**
67.	butyl benzyl phthalate	1.8×10^{10}**	1.8×10^{9}**	4.3×10^{10}**	1.2×10^{9}**	1.0×10^{11}**	3×10^{9}**
68.	di-n-butyl phthalate	5×10^{6}**	1×10^{6}**	1×10^{7}**	7.5×10^{5}**	1.8×10^{7}**	1.8×10^{6}**
69.	di-n-octyl phthalate	1.8×10^{10}***	2.5×10^{10}*	4×10^{10}**	1.9×10^{10}**	1.0×10^{11}**	2.2×10^{11}**
70.	diethyl phthalate	36000***	3500**	77000**	2600**	60000**	5000**
71.	dimethyl phthalate	3000***	210**	6200**	160**	4000**	310**
72.	1,2-benzanthracene	7×10^{5}***	4.8×10^{6}*	3×10^{6}*	3.5×10^{6}*	1.7×10^{7}*	3.7×10^{7}*
73.	benzo (a) pyrene (3,4-benzopyrene)	3×10^{6}***	2.4×10^{7}*	1×10^{7}*	1.8×10^{7}*	1.7×10^{7}*	3×10^{8}*
74.	3,4-benzofluoranthene	4.6×10^{6}***	9.8×10^{6}*	8×10^{6}*	6.9×10^{6}*	5.6×10^{7}*	6.6×10^{7}*
75.	11,12-benzofluoranthene	4.6×10^{6}***	9.8×10^{6}*	8×10^{6}*	6.9×10^{6}*	5.6×10^{7}*	6.6×10^{7}*
76.	chrysene	7×10^{5}***	6×10^{5}*	1×10^{6}*	4.1×10^{5}*	1.1×10^{7}*	2×10^{6}*
77.	acenaphthylene	1700***	11000*	9000*	9100*	3300*	1×10^{5}*
78.	anthracene	40000***	18000*	12000*	12000*	6×10^{5}*	4.7×10^{4}*
79.	1,12-benzoperylene	1.4×10^{6}***	240,000*	7×10^{5}*	1.2×10^{5}*	5.4×10^{8}*	4.3×10^{5}*
80.	fluorene	20000***	6600*	18000*	4700*	1.9×10^{5}*	1.6×10^{4}*

I.D. Compound	Isobutane	n butyl acetate	Isobutyl acetate	Di isopropyl ether	Octanol
66. bis(2-ethylhexyl) phthalate[1]	$3.5\times10^{9**}$	$6\times10^{10**}$	$5.5\times10^{10**}$	$3.2\times10^{10**}$	$7.1\times10^{9(12)}$
67. butyl benzyl phthalate	$1.3\times10^{9**}$	$4.3\times10^{10**}$	$3.7\times10^{10**}$	$1.9\times10^{10**}$	$4.8\times10^{9(12)}$
68. di-n-butyl phthalate	$8\times10^{5**}$	$9.7\times10^{6**}$	$8.5\times10^{6**}$	$4.8\times10^{6**}$	$2.6\times10^{6(12)}$
69. di-n-octyl phthalate	$1.2\times10^{11**}$	$2.8\times10^{10**}$	$3.7\times10^{10**}$	$7.8\times10^{10**}$	$4.8\times10^{9(12)}$
70. diethyl phthalate	2400^{*}	81000^{**}	66000^{*}	20000^{*}	$26300^{(12)}$
71. dimethyl phthalate	150^{**}	6600^{**}	5380^{**}	1400^{**}	$2630^{(12)}$
72. 1,2-benzanthracene	$2\times10^{7*}$	$3.7\times10^{6*}$	$3.4\times10^{6*}$	$7.2\times10^{6*}$	$4.1\times10^{5(12)}$
73. benzo (a) pyrene (3,4-benzopyrene)	$2\times10^{8*}$	$7.4\times10^{6*}$	$1\times10^{7*}$	$3.7\times10^{7*}$	$1.6\times10^{6*}$
74. 3,4-benzofluoranthene	$6.3\times10^{6*}$	$6.3\times10^{6*}$	$7.7\times10^{6*}$	$1.4\times10^{7*}$	$2.3\times10^{6*}$
75. 11,12-benzofluoranthene	$6.3\times10^{6*}$	$6.3\times10^{6*}$	$7.7\times10^{6*}$	$1.4\times10^{7*}$	$2,3\times10^{6*}$
76. chrysene	$1.1\times10^{6*}$	$8.9\times10^{5*}$	$9\times10^{5*}$	$9.5\times10^{5*}$	$4.1\times10^{5(12)}$
77. acenaphthylene	8100^{*}	4900^{*}	7000^{*}	$2.2\times10^{4*}$	1570^{*}
78. anthracene	$2.6\times10^{4*}$	$4.2\times10^{4*}$	$4\times10^{4*}$	$3.2\times10^{5*}$	$2.8\times10^{4(9)(13)}$
79. 1,12-benzoperylene	$1.2\times10^{5*}$	$7.9\times10^{5*}$	$6\times10^{5*}$	$2.4\times10^{5*}$	$7.9\times10^{5*}$
80. fluorene	8800^{*}	$1.8\times10^{4*}$	$1.7\times10^{4*}$	$1.3\times10^{4*}$	$1.5\times10^{4(9)}$

I.D. Compound	Cumene	Mesityl oxide	MEK	ethyl acetate	Ethyl ether	Ethyl benzene	n-hexanal
66. bis(2-ethylhexyl) phthalate	$2.5x10^{11**}$	$6x10^{10**}$	$6.2x10^{10**}$	$4.6x10^{10**}$	$8.7x10^{10**}$	$1x10^{11**}$	$1.1x10^{9**}$
67. butyl benzyl phthalate	$1.6x10^{11**}$	4x10**	$4x10^{10**}$	$2.9x10^{10**}$	$4x10^{10**}$	$7x10^{10**}$	$1.1x10^{9**}$
68. di-n-butyl phthalate	$3.3x10^{7**}$	$9.6x10^{6**}$	$9.3x10^{6**}$	$7.2x10^{6**}$	$1x10^{7**}$	$6x10^{6**}$	$6.2x10^{5}$
69. di-n-octyl phthalate	$2.6x10^{10**}$	$2.8x10^{10**}$	$4.3x10^{10**}$	$3.8x10^{10**}$	$1.7x10^{11**}$	$1.5x10^{11**}$	$1.5x10^{9***}$
70. diethyl phthalate	$1.1x10^{5**}$	$9.6x10^{6**}$	$1x10^{5**}$	83000**	50000**	28000**	15000**
71. dimethyl phthalate	6600**	8200**	9800**	7600**	3600**	2000**	2000**
72. 1,2-benzanthracene	$5.2x10^{6*}$	$2x10^{6*}$	$1.7x10^{6*}$	$1.7x10^{6*}$	$1x10^{7*}$	$1x10^{7*}$	$8.9x10^{4*}$
73. benzo (a) pyrene (3,4-benzopyrene)	$8.6x10^{6*}$	$5.3x10^{6*}$	$5.3x10^{6*}$	$5.8x10^{6*}$	$5.2x10^{7*}$	$1.3x10^{7*}$	$4.9x10^{5*}$
74. 3,4-benzofluoranthene	$1.5x10^{7*}$	$4.6x10^{6*}$	$3.9x10^{6*}$	$3.8x10^{6*}$	$2.1x10^{7*}$	$3x10^{7*}$	$2.2x10^{5*}$
75. 11,12-benzofluoranthene	$1.5x10^{7*}$	$4.6x10^{6*}$	$3.9x10^{6*}$	$3.8x10^{6*}$	$2.1x10^{7*}$	$3x10^{7*}$	$2.2x10^{5*}$
76. chrysene	$2.7x10^{7*}$	$7.1x10^{5*}$	$5.6x10^{5*}$	$5x10^{5*}$	$1.4x10^{6*}$	$4.9x10^{6*}$	$8.5x10^{4*}$
77. acenaphthylene	3550*	4000*	4480*	5000*	$2.5x10^{4*}$	3320*	4580
78. anthracene	$1.4x10^{5*}$	$3.5x10^{4*}$	$2.6x10^{4*}$	$2.3x10^{4*}$	$4.6x10^{4*}$	$2.4x10^{5*}$	6000*
79. 1,12-benzoperylene	$1.5x10^{7*}$	$5.5x10^{5*}$	$2.8x10^{5*}$	$2x10^{5*}$	$5.4x10^{5*}$	$8.5x10^{7*}$	$2.9x10^{4*}$
80. fluorene	$5.6x10^{4*}$	$1.5x10^{4*}$	$1.2x10^{4*}$	$1x10^{4*}$	$1.8x10^{4*}$	$8x10^{4*}$	3570*

Estimation of Emissions from Storage Tanks

Storage tanks have been serving the petroleum and chemical industries for storing large volume of organic compound. Handling of hazardous wastes may require some type of storage. Hazardous materials are more safely handled and stored in closed systems. Vented storage will result in emissions of volatile toxic chemicals. The quantity of the emissions will be dependent upon design of the facility, physical and chemical characteristics of the material stored, and type of control.

It is not unusual to find fixed-roof storage tanks storing petroleum compounds with true vapor pressures less than 1.5 psia, and floating-roof tanks storing petroleum and petrochemical liquids with true vapor pressures ranging from 1.5 psia to 11 psia. When a volatile liquid with true vapor pressures greater than 11 psia is stored, a vapor recovery system is commonly used to prevent excessive emissions.

Hazardous wastes could be treated in storage facilities. The treatment process may employ chemical or physical means which will accompany emissions of hazardous air pollutants into the atmosphere. Understanding of the nature of resulting emissions would require a thorough knowledge on the type and degree of chemical reactions being carried out, and the accompanying physical progresses.

.When the emission rate of a hazardous air pollutant under consideration is substantial, the vapor phase may not be in equilibrium with the liquid phase due to resistance in the gas or liquid phase, and the emission rate can be mass-transfer controlled. The calculation of the emission rate from this type of storage as often be encountered in storing hazardous waste sludges will require consideration of mass transfer rates. The methodology developed for surface impoundments and pan evaporation will be applicable in this case. The overall mass transfer coefficient needed in the emission rate equation may be obtained from the individual liquid and gas phase mass transfer coefficients, and the vapor liquid equilibrium constant which can be estimated using the method described later. The individual mass transfer coefficients can be obtained from the correlations presented in the manual prepared for estimating emissions from surface impoundments (18).

Description of Storage Tanks

Three types of tank design will be considered in connection with estimating emissions from storage of liquid organic compounds: fixed roof, external floating roof, and internal floating roof. Although the latter two types can be considered a variation of a floating roof design, the distinction is made to differentiate air emission mechanism and estimation method.

1. Fixed Roof Tanks: Fixed roof storage tanks consist of a vertical cylindrical shell for storing

liquid compounds and a conical top for closure. The conical top is normally sloped. A pressure-vacuum vent installed on the upper part of the tank relieves changes in pressure in the volume space inside the tank. Vapors relieved from the vapor space in contact with stored liquid are released to the atmopshere as emissions.

2. External Floating Roof Tanks: These tanks are often called open type floating roof tanks. Both external and internal floating roof tanks utilize the similar design for construction of floating roofs. Floating roofs float on the top surface of the tank liquid, and slide up and down as liquid is filled or withdrawn. To prevent the exposure of the liquid to the atmosphere, the roofs are equipped with primary and secondary seals designed to maintain a tight gap between the seal and the tank shell wall. Floating roofs are exposed to the weather in the external floating roof tanks. Emissions from this type of tanks are mostly wind-induced. It is an efficient method of storing volatie liquids with minimum vapor loss, and is more efficient than a fixed roof tank with a vapor recovery system in reducing atmospheric emissions. It is reported that the gap between the tank shell and the seals have a significant effect on emission rates, the effect being more pronounced in foam-type seals than shoes.

3. Internal Floating Roof Tanks: Internal floating roof tanks,

also referred to as cover type floating roof tanks, are essentially external floating roof tanks with a fixed roof which covers the tank. The fixed roof protects the floating roof from the weather, and no provision is necessary for rain or snow removal, or for seal protection. The fixed roof act as a shield from the wind that penetrates a relatively large saturated gap space which provides a direct path for volatilization.

For external and internal floating roofs, primary seals are commonly shoe-type or foam-type, and secondary seals are flapper type which can be rim-mounted or shoe-mounted. Rim-mounted secondary seals are preferred to the shoe-mounted secondary seals in reducing emissions. Secondary seals are effective in reducing wind-induced losses.

Method of Estimating The Emission of a Volatile Chemical

The methodology used in estimating emissions of specific types of hazardous pollutants from storage tanks consists of estimating the emission of total organic compounds and the concentration of a particular compound in the organic vapor phase. If the compound in storage is not a mixture but is a pure liquid, it is not necessary to correct for the concentration in the vapor phase, and the estimated hydrocarbon emission corresponds to the emission of the compound under consideration.

In 1960's, the American Petroleum Institute presented empirical formulae for use in estimating the emissions of total hydrocarbons from storage operations. Bulletin 2517(1), Bull. 2518(2), and Bull. 2519(4) cover fixed roof tanks, external floating roof tanks, and internal floating roof tanks, respectively. In 1970's, the American Petroleum Institute(API) in cooperation with Chicago

Bridge and Iron Company(CBI) conducted extensive testing of pilot and commercial scale external floating roof storage tanks to verify the method in Bulletin 2518 and AP-42(5). The study included quantification of the effect of several variables on double seal floating roof standing loss emissions.

The results of the study are incorporated in the revised publication, Bulletin 2517 published in 1980(6). Subsequently, AP-42 was revised, and its supplement 12 included the updated empirical formula in accordance with Bull. 2517. The methods in API Bulletin 2518 and Bulletin 2519 are also being considered for revision. The draft revision of Bulletin 2519 is expected to be available for review early part of 1982. Until the study is completed, the methods used here are taken from the API bulletins and AP-42 for emissions from fixed roof and internal floating roof storage tanks.

In addition to the estimation of total hydrocarbon emissions, it is necessary to estimate the concentration of a particular compound present in the emissions. The estimation requires consideration of vapor-liquid equilibrium and evaluation of the equilibrium constant. Among a number of ways of obtaining the value of equilibrium constant, engineering techniques are summarized in the appendix of the manual developed for estimating emissions from land disposal facilities. A simplified method will be enumerated in this procedure. A more elaborate procedure for calculating the vapor-liquid equilibrium constant can be found by consulting the references cited.

Emissions

AP-42 (3) reports six major sources of emissions from storage tank operations. 1) For fixed-roof storage tanks, the source of evaporation loss includes breathing losses and working losses. 2) For floating roof storage tanks, the source of loss includes standing storage losses and withdrawal losses.

Fixed roof breathing loss results from discharge of vapors from the tank volume due to variation of its internal pressure and storage temperature. Expansion of the vapor volume causes to expel existing vapors from the tank, thus relieving excessive pressure build-up.

Fixed-roof working loss results from displacement of liquid level as liquid level ascends or descends during filling or emptying operations. Filling loss is the loss of vapor amounting to the input of liquid. The emptying loss results from discharge of vapors from the tank subsequent to withdrawal of its content during emptying operations, and is attributable to the intake air volume saturated with organic liquids in the tank.

Floating roof standing storage losses consist of vapor lost during storage in the absence of liquid displacement in the tank. Loose fit of primary and secondary seals are considered to be a major cause of the loss. The study by CBI showed that the standing loss emissions for external floating roofs are attributable to wind effect, rim heating effect, variation in storage temperature, and change in barometric pressure.

It is indicated that vapor permeation through the seals is the cause of additional vapor loss. Apparently, this phenomena is more pronounced when storing pure chemicals. The correlation presented in Supplement 12 of AP-42 does not take into consideration the effect of permeabilities of the seals. It is being investigated to include this effect to account for part of the increased loss of pure chemicals indicated by actual measurements in comparison with the loss calculated by Supplement 12 of AP-42.

Floating roof withdrawal loss results from volatilization of liquid material clinging to the wall as the floating roof travels downward during withdrawal operations. This is also called wall wetting loss. The wall wetting effect is considered insignificant compared to standing storage losses.

Conversion To Petrochemical Losses

Losses of petrochemicals from storage tanks can be calculated by using "gasoline" as a reference by one of the following two methods:

1. API method of conversion (Reference 7)
2. AP-42 method of conversion

1. API method

This method uses a hypothetical gasoline under the same storage conditions. But the true vapor pressure of the chemical being stored should be used in the estimation equation. The true vapor pressure for a pure chemical equals the vapor pressure at the storage conditions. The true vapor pressure for a petrochemical mixture is a summation of partial pressures of each component in equilibrium with the stored liquid at the operating temperature and pressure. The loss estimated for the hypothetical gasoline is multiplied by

$$\frac{0.08\,M_p}{W_p} \tag{1}$$

where M_p: molecular weight of stored petrochemical

W_p: density of stored chemical, lb/gal.

2. AP-42 method

AP-42 recommends use of a true gasoline under the same storage conditions, including the true vapor pressure of gasoline, times a value to get

$$L_p = 0.08 \frac{M_p}{W_G} \frac{P_p}{P_G} L_G \qquad (2)$$

where L_p, L_G = losses of petrochemical(p) and gasoline(G), lb/day-10^3 gal

M_p = molecular weight of petrochemical(p), lb/mol

W_G = liquid density of gasoline, lb/gal

P_p, P_G = true vapor pressures of petrochemical(p) and gasoline(G) at their bulk storage temperature, psia.

When the values for W_G and P_G are substituted, Equation (2) becomes

$$L_p = 0.08 \frac{M_p}{6.2} \frac{P_p}{11} = 1.173\times10^{-3} M_p P_p L_G \qquad (3)$$

Storage Loss Formula (6)

Fixed roof tank breathing losses can be estimated from :

$$L_B = 2.26 \times 10^{-2} M \left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73} H^{0.51} \Delta T^{0.50} F_p C K_C \qquad (4)$$

where: L_B = fixed roof breathing loss (lb/year)

M = molecular weight of vapor in storage tank (lb/lb mole). See Table 1.

P = true vapor pressure at bulk liquid conditions (psia). See Note 1

D = tank diameter (ft)

H = average vapor space height, including roof volume correction (ft). See Note 2

ΔT = average ambient diurnal temperature change (°F)

F_P = paint factor (dimensionless). See Table 2.

C = adjustment factor for small diameter tanks (dimensionless). See Figure 1.

K_C = product factor (dimensionless). See Note 3

Notes: (1) True vapor pressures for organic liquids can be determined from Figures 2 or 3. or Table 1.
(2) The vapor space in a cone roof is equal in volume to a cylinder which has the same base diameter as the cone and is one third the height of the cone
(3) For crude oil, K_C = 0.65
For all other organic liquids, K_C = 1.0

Definitions

True vapor pressure: the equilibrium partial pressure exerted by a volatile organic liquid as defined by ASTM-D-2879 or as obtained from standard reference texts.

Reid vapor pressure: the absolute vapor pressure of volatile crude oil and volatile nonviscous petroleum liquids, except liquified petroleum gases, as determined by ASTM-D-323-58.

Fixed roof tank working losses can be estimated from :

$$L_W = 2.40 \times 10^{-2} MPK_NK_C \qquad (5)$$

where: L_W = fixed roof working loss (lb/10^3 gal throughput)

M = molecular weight of vapor in storage tank (lb/lb mole). See Table 1.

P = true vapor pressure at bulk liquid conditions (psia). See Note 1

K_N = turnover factor (dimensionless). See Figure 4.

K_C = product factor (dimensionless). See Note 2

Notes: (1) True vapor pressures for organic liquids can be determined from Figures 2 or 3 , or Table 1
(2) For crude oil, K_C = 0.84
For all other organic liquids, K_C = 1.0

The fixed roof working loss (L_W) is the sum of the loading and unloading losses. Special tank operating conditions may result in losses which are significantly greater or lower than the estimates provided by Equation 5.

TABLE 1. PHYSICAL PROPERTIES OF TYPICAL ORGANIC LIQUIDS

Organic Liquid*	Vapor molecular weight @ 60°F	Product density (d), lb/gal @ 60°F	Condensed vapor density (w), lb/gal @ 60°F	True vapor pressure in psia at:						
				40°F	50°F	60°F	70°F	80°F	90°F	100°F
Petroleum Liquids										
Gasoline RVP 13	62	5.6	4.9	4.7	5.7	6.9	8.3	9.9	11.7	13.8
Gasoline RVP 10	66	5.6	5.1	3.4	4.2	5.2	6.2	7.4	8.8	10.5
Gasoline RVP 7	68	5.6	5.2	2.3	2.9	3.5	4.3	5.2	6.2	7.4
Crude oil RVP 5	50	7.1	4.5	1.8	2.3	2.8	3.4	4.0	4.8	5.7
Jet naphtha (JP-4)	80	6.4	5.4	0.8	1.0	1.3	1.6	1.9	2.4	2.7
Jet kerosene	130	7.0	6.1	0.0041	0.0060	0.0085	0.011	0.015	0.021	0.029
Distillate fuel No. 2	130	7.1	6.1	0.0031	0.0045	0.0074	0.0090	0.012	0.016	0.022
Residual oil No. 6	190	7.9	6.4	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.00019
Volatile Organic Liquids										
Acetone	58	6.6	6.6	1.7	2.2	2.9	3.7	4.7	5.9	7.3
Acrylonitrile	53	6.8	6.8	0.8	1.0	1.4	1.8	2.4	3.1	4.0
Benzene	78	7.4	7.4	0.6	0.9	1.2	1.5	2.0	2.6	3.3
Carbon disulfide	76	10.6	10.6	3.0	3.9	4.8	6.0	7.4	9.2	11.2
Carbon tetrachloride	154	13.4	13.4	0.8	1.1	1.4	1.8	2.3	3.0	3.8
Chloroform	119	12.5	12.5	1.5	1.9	2.5	3.2	4.1	5.2	6.3
Cyclohexane	84	6.5	6.5	0.7	0.9	1.2	1.6	2.1	2.6	3.2
1, 2-Dichlorethane	99	10.5	10.5	0.6	0.8	1.0	1.4	1.7	2.2	2.8
Ethylacetate	88	7.6	7.6	0.6	0.8	1.1	1.5	1.9	2.5	3.2
Ethyl alcohol	46	6.6	6.6	0.2	0.4	0.6	0.9	1.2	1.7	2.3
Isopropyl alcohol	60	6.6	6.6	0.2	0.3	0.6	0.7	0.9	1.3	1.8
Methyl alcohol	32	6.6	6.6	0.7	1.0	1.4	2.0	2.6	3.5	4.5
Methylene chloride	85	11.1	11.1	3.1	4.3	5.4	6.8	8.7	10.3	13.3
Methylethyl ketone	72	6.7	6.7	0.7	0.9	1.2	1.5	2.1	2.7	3.3
Methylmethacrylate	100	7.9	7.9	0.1	0.2	0.3	0.6	0.8	1.1	1.4
1, 1, 1-Trichloroethane	133	11.2	11.2	0.9	1.2	1.6	2.0	2.6	3.3	4.2
Trichloroethylene	131	12.3	12.3	0.5	0.7	0.9	1.2	1.5	2.0	2.0
Toluene	92	7.3	7.3	0.2	0.2	0.3	0.4	0.6	0.8	1.0
Vinylacetate	86	7.8	7.8	0.7	1.0	1.3	1.7	2.3	3.1	4.0

S = stripping factor, KV/L

Sc = Schmidt number

T = temperature, °K

V = superficial vapor rate, kg/s

V_a = vapor velocity through active tray area, m/s

x = liquid phase mole fraction

y = gas-phase composition, mole fraction

Z = column height, m

Z_L = length of liquid travel across tray, m

z = average liquid flow width on a tray, m

GREEK LETTERS

α, β = empirical constants in Equation (27)

γ = activity coefficient

ρ = density, kg/m^3

θ_L = liquid residence time on tray, s

μ_L = liquid viscosity, Pa·s

SUBSCRIPT

G = gas-phase

i = component i, or influent wherever defined

L = liquid-phase

n = nth stage

o = effluent

SUPERSCRIPT

$*$ = composition in equilibrium with other phase

∞ = infinite dilution

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II. SOLVENT EXTRACTION

The extraction of organic pollutants involves knowledge of the distribution coefficients and mass-transfer rates for a wide range of solvents, and organic solute compounds which may be treated simultaneously. Since the literature data on the distribution coefficients andd mass-transfer rates are limited, it has been necessary to simplify a true thermodynamic model and transport model by working with average values for the wide range of solutes and solvents. Most literature studies on extraction column operations were presented with the primary goal of extracting a generalized correlation obtained using a chosen solute-solvent system rather than to obtain a set of data for the system involving the organic pollutants. Therefore the methodology may be used to estimate the extraction capability for pollutant-solvent pairs not tested experimentally.

Distribution Coefficients

The design of an extractor for removal of organic pollutants from waste requires knowledge of distribution of the pollutants between the waste feed and solvent phases. A common method of characterizing the distribution is the use of distribution coefficient defined as

$$K_x = \frac{x_o}{x_w} \qquad (1)$$

where K_x is the distribution coefficient in units of (mole fraction of organic pollutant in solvent phase (o) /mole fraction of organic pollutant in waste phase (w)), and x is the mole fraction of the pollutant.

A solvent with a larger distribution coefficient can achieve more efficient separation, thus requiring less solvent per unit volume of waste treated at a given degree of extraction. For dilute aqueous and solvent solutions, the thermodynamic equation relating the two phases is

$$K_x = \frac{\gamma_w^{\infty}}{\gamma_o^{\infty}} \tag{2}$$

where γ_w^{∞} and γ_o^{∞} are the infinite dilution activity coefficients of the organic pollutant in water and solvent phases, respectively. The application of solvent extraction to waste water generally has been limited to removal of phenol and phenolic compound present at high concentration.

An alternate way of representing the distribution coefficient is in terms of weight fraction or concentration defined as

$$K_d = \frac{\text{g solute/1000 g solvent}}{\text{g solute/1000 g waste}} ,$$

and

$$K_v = \frac{\text{g solute/1000 ml solvent}}{\text{g solute/1000 ml waste}}$$

K_x, Kd, and Kv are related as

$$K_v = K_d \frac{\rho_s}{\rho_w} = K_x \frac{MW_w}{MW_s} \frac{\rho_s}{\rho_w} \tag{3}$$

where ρ is the specific gravity in gr/cc, and MW is the molecular weight.

A solvent that is volatile and les soluble in waste is attractive from the standpoint of minimizing solvent loss and of easy removal from the contaiminated waste by steam stripping or distillation. but it is important for good extraction that the distribution coefficient of the volatile solvent be as large as possible. The solvents commonly used for extraction of phenol an phenolic compounds from wastewater are di-isopropyl either and n-butyl acetate. Several alternative polar and nonpolar solvents are reported in the literature.

A large number of distribution coefficients can be found in the literature for various solute-solvent pairs. For the organic pollutants, however, the experimental values may be limited. If the experimental or literature values are lacking, they can be calculated using the thermodynamic relationships.

The experimental and calculated distribution coefficients between water and selected solvents, K_v, are collected in Table 1(1).

Sometimes two solvents are mixed to obtain desirable solvent properties in viscosity and density. The distribution coefficient for an organic pollutant distributing between the solvent mixture and waste can be approximated by

$$(K_v)_m = x_1(K_v)_1 + x_2(K_v)_2 \qquad (4)$$

where $(K_v)_m$ is the distribution coefficient in the solvent mixture, x_1 is the volume fraction of solvent 1, or volume of solvent 1/(volume of solvent 1 + volume of solvent 2), x_2 is the volume fraction of solvent 2, and $(K_v)_1$ and $(K_v)_2$ is the distribution coefficients in pure solvent 1 and solvent 2, respectively, in units of gr solute/1000 cc solvent.

Solvent Extraction Column

Solvent extraction can be carried out in multistage equilibrium equipment, packed columns, tray columns, spray towers, or agitated contactors. The flowsheet for separation by the different liquid extraction equipment, and sketches of extractor internals are described in various reviews (2), (3), (4), (5). Choosing the most suitable extractor is the problem of design for a liquid-liquid extraction system.

Misek and Rod, in their review of liquid-liquid extraction, describe various models which accout for longitudinal mixing. The design procedure recommended by Treybal (4),(5) neglects the effect of axial mixing in the continuous extractor, but appears to provide conventional calculation methods.

The equilibrium stage would theoretically chieve the maximum efficiecy for extraction. However, the actual performance is influenced by the method of proper mixing and settling, which in turn influences the extraction rate. For multistage equilibrium extractors, the fraction of a given organic pollutant removed, f, can be represented by the Kremser equation:

$$f = \frac{E^{N+1} - E}{E^{N+1} - 1} \qquad (5)$$

wher E is the extraction factor defined by $E = K_v V_s/V_w$, N is the number of theoretical stages, K_v is the distribution coefficient as defined by Equation (3), and V_s and V_w are volumetric flow rates of solvent and waste, respectively. In deriving Equation (5), it is assumed that the solvent feed to each stage is free of the organic pollutants.

Underlying principles in solvent extraction using packed columns is analogous to steam stripping-namely, the use of packing, the use of extraction factor similar to stripping factor, evaluation of the number of transfer units and the height of a transfer unit.

The treatment similar to the derivation for steam stripping design (1) is applicable to the problem of solvent extraction in packed towers. The expression for the packed column extractor design is

$$Z = HTU_{ox} \frac{1}{1 - \frac{1}{E}} \ln \frac{x_2(1 - \frac{1}{E}) + \frac{1}{E} x_1 - \frac{1 - \eta}{\eta} \frac{1}{E} (x_2 - x_1)}{x_1 - \frac{1 - \eta}{\eta} \frac{1}{E} (x_2 - x_1)} \qquad (6)$$

where Z is the height of packing, m, E, is the extraction factor ($K_v V_s/V_w$), V_s and V_w are the superficial velocity of solvent and waste, respectively m/hr, x_2 and x_1 are the waste influent and effluent concentrations, respectively, mg/l, HTU_{ox} is the height of a transfer unit, m, and η is the fractional removal of the organic pollutant in the solvent purification step.

The height of a transfer unit related to that in the waste phase, H_x, and that in the solvent phase, Hy, by

$$HTU_{ox} = H_x + \frac{V_w}{K_v V_s} H_y \qquad (7)$$

Treybal summarizs some of the performance data obtained using continuous countercurrent packed tower extractors. Although the generalized correlation for the height of a transfer unit in terms of the individual film values is lacking, the representative values given for the empirical correlation in the Perry's Handbook are taken as follows:

$$H_x = 0.41 \left(\frac{V_w}{V_s} \right)^{0.73}, \text{m} \qquad (8)$$

$$H_y = 0.305 \text{ m} \qquad (9)$$

For a given solvent to waste ratio and fractional removal of toxic organics in the solvent purification step, the required heights of packing to achieve an effluent target can be calculated.

Although a solvent-to-waste ratio greater than 0.2 may not be considered an the economic standpoint, it can be reduced to a value considerably less than 0.2 in a system in which the distribution coefficients are very large. Also, the magnitude of the extraction factor is relatively insensitive to the degree of removal beyond a minimum value. For example, the extraction factors of 2, 80, 100, and 120 achieve the % removal of 97.2%, 99.88%, 99.88%, and 99.88% respectively; an extraction factor with $K_v = 4000$ at $V_s/V_w = 0.02$ achieves the same result as an extraction factor with $K_v = 400$ at $V_s/V_w = 0.2$, or $K_v = 4000$ and $V_s/V_w = 0.05$.

An expression describing perforated-tray liquid-liquid extraction towers can be represented by

$$N = \ln \frac{\frac{V_w}{V_s}\frac{1-\eta}{\eta} x_2 - \left(\frac{V_w}{V_s}\frac{1-\eta}{\eta} + K_v\right) x_1}{\left(\frac{V_w}{V_s}\frac{1}{\eta} - K_v\right) x_2 - \frac{V_w}{V_s}\frac{1}{\eta} x_1} \Bigg/ \ln\frac{1}{E} \qquad (10)$$

where N is the number of theoretical states required. The derivation of Equation (10) can be found in Reference 1.

The tray efficiency correlation originally presented by Treybal is modified by Murty (3), and is given by

$$E_o = 3.88 \times 10^5 \frac{H_{ps}^{0.5}}{\sigma} \left(\frac{V_s}{V_w}\right)^{0.42} \left(\frac{1}{d_o}\right)^{0.25} \qquad (11)$$

where E_o is the tray efficiency, Hps is the tray spacing, m, σ is the interfacial tension, N/m (Note 1 lb-mass/sq.hr = 28.7 N/m) and d_o is the perforated orifice diameter, m.

Table 1. Distribution Coefficients (K_v) of Organic Priority Pollutants in Various Solvents

I.D.	Compound	Tricresyl Phosphate	Undecane	MIBK	Tridecane	Benzene	Isobutylene	Isobutane	n butyl acetate	Isobutyl acetate	Di Isopropyl ether	Octanol
1.	acenaphthlene	16,700**	7400*	15000*	7800*	126000*	21700*	12600*	14000*	14000*	13700*	11400*
2.	acrolein	0.06**	0.8*	2.3*	0.8*	1.8*	1.4*	1*	2.3*	2.2*	0.9*	0.11**
3.	acrylonitrile	0.15**	0.5*	2.2*	0.4*	5*	1.1*	0.8*	2.2*	1.9*	0.8*	0.12(9)
4.	benzene	132**	166(9)	150*	40*	518.4(14)	242(3)	186(3)	54.2(3)(14)	54**	54**	1.35(11)
5.	benzidine	59**	52*	77*	44*	110*	140*	90*	66*	70*	80*	64(12)
6.	carbon tetrachloride (tertrachloromethane)	480**	380*	930*	300*	2200*	1200*	810*	870*	900*	990*	436(9)
7.	chlorobenzene	250*	260*	1200*	200*	2900*	685*	445*	1200*	1060*	460*	692(13)(9)
8.	1,2,4-trichlorobenzene	17,000*	12000*	20000*	10000*	66000*	15000*	10000*	19900*	19000*	14400*	18200(12)
9.	hexachlorobenzene	93,000*	290,000*	750,000*	200,000*	1×10^{7}*	68000*	37000*	7×10^{5}*	6.9×10^{5}*	5.2×10^{5}*	1.5×10^{6}(12)
10.	1,2-dichloroethane	31**	10*	38*	8*	100*	41.6(3)	24(3)	37*	36*	32*	30
11.	1,1,1-trichloroethane	81**	120*	220*	110*	270*	190*	150*	210*	210*	150*	92**
12.	hexachlorethane	11,000*	3500*	9600*	2500*	62000*	8600*	5300*	9400*	9000*	7600*	8800*
13.	1,1-dichloroethane	51*	56*	140*	52*	100*	94*	70*	140*	130*	68*	138*
14.	1,1,2-trichloroethane	74*	70*	220*	64*	200*	110*	80*	210*	200*	86*	224*

* estimated from solubility parameters.
** estimated using the method in reference 9.
*** estimated using the method in reference 3.

I.D. Compound	Cumene	Mesityl Oxide	MEK	ethyl Acetate	Ethyl ether	Ethyl benzene	n-hexanol	EDC	Toluene	Xylene	n-hexane
1. acenaphthlene	38800*	12000*	9680*	8980*	18900*	57600*	2200*	1.6×10^{5}*	75700*	91000*	20000*
2. acrolein	0.8*	2.9*	3.7*	3.4*	1.7*	1.6*	3.1*	0.8*	1.7*	2.8*	1*
3. acrylonitrile	1.9*	3.3*	5.3*	4.2*	1.6*	2.6*	3.5*	7.4*	3.2*	4.7*	1.1*
4. benzene	263*	130*	114*	109*	176*	218*	45*	473*	271*	360*	116*
5. benzidine	85*	66*	78*	70*	131*	86*	16*	65*	98*	136*	101*
6. carbon tetrachloride (tertrachloromethane)	1460*	770*	690*	668*	1200*	1266*	236*	2329*	1570*	2069*	866*
7. chlorobenzene	1080*	1700*	3480*	2360*	1000*	1450*	1180*	3700*	1660*	2500*	610*
8. 1,2,4-trichlorobenzene	35,000*	19900*	19600*	17000*	20000*	43000*	9090*	73000*	51000*	75700*	18400*
9. hexachlorobenzene	2.6×10^{6}*	6.3×10^{5}*	4.7×10^{5}*	4.2×10^{5}*	7.5×10^{5}*	4.2×10^{6}*	1.2×10^{5}*	1.9×10^{7}*	5.7×10^{6}	6.8×10^{6}*	8×10^{5}*
10. 1,2-dichloroethane	72*	34*	30*	28*	40*	55*	14*	142*	70*	92*	24*
11. 1,1,1-trichloroethane	196*	212*	221*	208*	239*	22*	96*	212*	248*	388*	177*
12. hexachlorethane	2.4×10^{4}*	8183*	6600*	6100*	1×10^{4}*	2.8×10^{4}*	1184*	9×10^{4}*	3.7×10^{4}*	4.7×10^{4}*	8600*
13. 1,1-dichloroethane	66*	163*	200*	186*	127*	93.*	130*	55*	101*	163*	73*
14. 1,1,2-trichloroethane	108*	256*	309*	278*	174*	165.*	202*	115*	184.*	290*	95*

I.D.	Compound	Tricresyl Phosphate	Undecane	MIBK	Tridecane	Benzene	Isobutylene	Isobutane	n butyl acetate	Isobutyl acetate	Di isopropyl ether	Octanol
15.	1,1,2,2-tetrachloroethane	75*	27*	85*	20*	590*	61*	37*	85*	80*	60*	86*
16.	chloroethane	28**	31*	62*	30*	43*	50*	40*	60*	60*	37*	$35^{(9)}$
17.	bis (chloroethyl) ether											
18.	bis (2-chloroethyl) ether	21*	19*	90*	17*	82*	36*	22*	90*	80*	24*	94*
19.	2-chloroethyl vinyl ether (mixed)	15**	35*	34*	31*	60*	57*	45*	30*	33*	44*	20*
20.	2-chloronaphthalene	33000**	2500*	28000*	2200*	29000*	5000*	2500*	29000*	25000*	8000*	24000*
21.	2,4,6-trichlorophenol	1374***	9***	4900***	9***	144***	27***	7***	2610***	4123***	1580***	$2400^{(9)}$
22.	parachlorometa cresol	188***	1.5***	667***	1.5***	25***	5***	1.2***	357***	563***	217***	$1260^{(9)}$
23.	chloroform (trichloromethane)	80**	46*	117*	44*	88*	36*	57*	116*	111*	56*	$93^{(9)},^{(13)}$
24.	2-chlorophenol	90.5***	0.9***	$432.2^{(14)}$	0.9***	15***	3***	0.7***	$255.8^{(14)}$	272***	105***	$141^{(9)}$
25.	1,2-dichlorobenzene	2700**	1900*	3800*	1600*	11000*	2300*	1600*	3800*	3500*	2300*	$2400^{(9)}$
26.	1,3-dichlorobenzene	2700**	2800*	4600*	2400*	13700*	3500*	2500*	4580*	4350*	3400*	$2400^{(9)}$
27.	1,4-dichlorobenzene	2800**	830*	2500*	600*	12600*	2000*	1260*	2400*	2300*	2000*	$2455^{(9)}$
28.	3,3-dichlorobenzidine	2600*	0.03*	1*	0.02*	9*	0.04*	0.02*	1.3*	0.8*	0.05*	$2290^{(12)}$
29.	1,1-dichloroethylene	1100**	1000*	1200*	900*	2750*	1200*	960*	1100*	1120*	1150*	999*

I.D. Compound	Cumene	Mesityl Oxide	MEK	ethyl acetate	Ethyl ether	Ethyl benzene	n-hexanol	EDC	Toluene	Xylene	n-hexane
15. 1,1,2,2-tetrachloroethane	229*	75*	60*	54*	82*	261*	22*	963*	340*	432*	66*
16. chloroethane	33*	67*	79*	75*	61*	40*	50*	25*	43*	70*	39*
17. bis (chloroethyl) ether											
18. bis (2-chloroethyl) ether	34*	114*	148*	129*	63*	64*	92*	38*	72*	110*	28*
19. 2-chloroethyl vinyl ether (mixed)	49*	26*	23*	23*	54*	50*	6*	45*	56*	86*	50*
20. 2-chloronaphthalene	1.6x10^{4}*	3.7x10^{4}*	4.9x10^{4}*	41000*	1.9x10^{4}*	2x10^{4}*	3.8x10^{4}*	1x10^{4}*	2.3x10^{4}*	3.5x10^{4}*	4000*
21. 2,4,6-trichlorophenol	1650***	2540***	2950***	4027***	3721***	200***	1980***	322***	89***	70***	7***
22. parachlorometa cresol	225***	348***	404***	550***	372***	34***	270***	56***	16***	12***	1.2***
23. chloroform (trichloromethane)	56*	134*	162*	150*	103*	79*	109*	48.3*	86*	138*	60*
24. 2-chlorophenol	110***	200***	200***	265***	179***	20.***	130***	32***	9***	7***	0.7***
25. 1,2-dichlorobenzene	5970*	4000*	4057*	3560*	3400*	7327*	2248*	1.2x10^{4}*	5670*	1.3x10^{4}*	2880*
26. 1,3-dichlorobenzene	7800*	4560*	4500*	4047*	4660*	9295*	2240*	1.5x10^{4}*	1x10^{4}*	1.6x10^{4}*	4280*
27. 1,4-dichlorobenzene	5800*	2170*	1788*	1656*	2570*	6000*	673*	1.8x10^{4}*	7766*	9.9x10^{3}*	1968*
28. 3,3-dichlorobenzidine	1*	4*	10*	6*	6.2*	3*	17*	30*	3*	4*	0.09*
29. 1,1-dichloroethylene	1900*	990*	870*	840*	1360*	2127*	359*	2770*	2400*	3800*	1330*

I.D.	Compound	Tricresyl Phosphate	Undecane	MIBK	Tridecane	Benzene	Isobutylene	Isobutane	n butyl acetate	Isobutyl acetate	Diisopro	Octanol
30.	1,2-trans-dichloroethylene	770**	260*	840*	210*	1500*	710*	510*	810*	810*	830*	738*
31.	2,4-dichlorophenol	304***	3***	1080***	3***	46***	9***	3***	580***	911***	351***	$562^{(12)}$
32.	1,2-dichloropropane	120*	125*	330*	114*	275*	200*	150*	320*	340*	150*	305*
33.	1,3-dichloropropylene (1,3-dichloropropene)	120*	130*	450*	120*	370*	230*	160*	450*	420*	150*	474*
34.	2,4-dimethylphenol	212***	4***	750***	4***	55***	.10***	2.7***	402***	635***	245***	420***
35.	2,4-dintrotoluene	90**	750*	1300*	620*	4000*	1000*	690*	1260*	1800*	940*	$102^{(12)}$
36.	2,6-dinitrotoluene	100**	"	1300*	"	"	"	"	"	"	"	$112^{(12)}$
37.	1,2-diphenylhydrazine	14***	0.2*	0.5*	0.14*	8*	0.6*	0.3*	0.4*	0.4*	0.3*	$19^{(12)}$
38.	ethylbenzene	1300*	660*	1200*	490*	5700*	2060*	1300*	1200*	1200*	1200*	$1412^{(11)}$
39.	fluroanthene	64,000*	570,000*	730,000*	430,000*	2.4×10^{6}*	2.6×10^{6}*	1.7×10^{6}*	6.3×10^{5}*	7.1×10^{5}	1×10^{6}*	3.4×10^{5}*
40.	4-chlorophenyl phenyl ether	610**	1400*	1500*	1000*	11000*	7300*	4100*	1200*	1600*	2100*	596*
41.	4-bromophenyl phenyl ether	380*	180*	440*	120*	14000*	440*	210*	430*	390*	270*	388*

I.D.	Compound	Cumene	Mesityl oxide	MEK	ethyl acetate	Ethyl ether	Ethyl benzene	n-hexanol	EDC	Toluene	Xylene	n-hexane
30.	1,2-trans-dichloroethylene	1300	738	665	640	982	903	294	1768	1100	1488	562
31.	2,4-dichlorophenol	364***	560***	650***	890***	600***	62***	437***	102***	28***	22***	3***
32.	1,2-dichloropropane	170	369	440	404	296	234	250	158.8	259	407	170.5
33.	1,3-dichloropropylene (1,3-dichloropropene)	168	555	703	632	333	315	492	180	246.8	548	178.8
34.	2,4-dimethylphenol	254***	390***	455***	621***	419***	76***	305***	124***	34.***	27***	2.5$^{(9)}$
35.	2,4-dintrotoluene	2250	1265	1268	1120	1360	2737	530	4400	3200	4700	1220
36.	2,6-dinitrotoluene	2250	1265	1268	1120	1360	2737	530	4400	3200	4700	1220
37.	1,2-diphenylhydrazine	1.6	0.36	0.27	0.24	0.5	2.9	0.057	11.9	3.9	4.6	0.6
38.	ethylbenzene	2480	995	840	797	1570	2940	230	6070	3700	4700	1400
39.	fluroanthene	$1x10^6$	$5.2x10^5$	$4.6x10^5$	$4.6x10^5$	$1.4x10^6$	$1.4x10^6$	$7.2x10^4$	$1.8x10^6$	$1.8x10^6$	$2.2x10^6$	$1.5x10^6$
40.	4-chlorophenyl phenyl ether	3000	972	808	784	3178	5670	73	8500	7300	8300	4500
41.	4-bromophenyl phenyl ether	2090	349	243	211	437	4630	46	$2.7x10^4$	6580	7400	582

I.D. Compound	Tricesyl Phosphate	Undecane	MIBK	Tridecane	Benzene	Isobutylene	Isobutane	n butyl acetate	Isobutyl acetate	Di isopropyl ether	Octanol
42. bis(2-chloroisoprophyl) ether	162**	430*	430*	360*	850*	980*	680*	350*	410*	630*	176*
43. bis(2-chloroethoxy) methane	7*	9*	9*	8*	15*	26*	17*	6*	18*	14*	3*
44. methylene chloride (dichloromethane)	13*	15*	50*	12*	106*	36*	26*	50*	46*	24*	72*
45. methyl Chloride (chloromethane)	9*	10*	18*	9*	14*	14*	11*	18*	17*	11*	30*
46. methyl bromide (bromomethane)	432*	460*	960*	450*	750*	680*	550*	960*	930*	530*	1000*
47. bromoform (tribromomethane)	143*	140*	530*	130*	500*	240*	160*	540*	490*	160*	610*
48. dichlorobromomethane	22*	22*	42*	20*	50*	36*	27*	42*	59*	27*	63*
49. trichlorofluro-methane	563*	690*	980*	650*	770*	1120*	950*	939*	955*	850*	740*
50. dichlorodifluro methane	2400*	7400*	6700*	6000*	5300*	38000*	33000*	5000*	6330*	15000*	4500*

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I.D. Compound	Cumene	Hedityl oxide	HEK	ethyl Acetate	Ethyl ether	Ethyl benzene	n- hexangl	EDC	Toluene	Xylene	n- hexane
42. bis(2-chloroisoprophyl) ether	656*	287*	256*	253*	881*	662*	31*	518.7*	751*	1066*	763*
43. bis(2-chloroathoxy) methane	12.*	5*	5*	5*	21*	12*	0.4*	8*	14*	19*	18*
44. methylene chloride (dichloromethane)	46*	69*	106*	89*	45*	59*	58*	134*	68*	103*	30*
45. methyl Chloride (chloromethane)	10*	20*	24*	22*	16*	14*	20*	9*	15*	24*	11*
46. methyl bromide (bromomethane)	509*	1090*	1300*	1220*	846*	700*	1049*	434*	751*	1249*	550*
47. bromoform (tribromomethane)	208*	482*	880*	778*	366*	418*	696*	238*	462*	734*	188*
48. dichlorobromomethane	30*	73*	89*	81*	52*	44*	61*	28*	48*	77*	29*
49. trichlorofluro- methane	701*	925*	1000*	975*	1200*	318*	454*	503*	773*	1249*	894*
50. dichlorodifluro methane	5127*	4180*	4600*	23000*	2.1×10^4*	4573*	269*	2578*	4500*	7380*	14880*